

THESIS

SOURCES, OCCURRENCE, AND MOBILIZATION
OF SELENIUM IN COLORADO'S LOWER
ARKANSAS RIVER VALLEY

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WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY BRENT M. CODY ENTITLED SOURCES, OCCURRENCE, AND MOBILIZATION OF SELENIUM IN COLORADO'S LOWER ARKANSAS RIVER VALLEY BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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ABSTRACT OF THESIS

SOURCES, OCCURRENCE, AND MOBILIZATION OF SELENIUM IN COLORADO'S LOWER ARKANSAS RIVER VALLEY

The accumulation of selenium (Se) in water bodies and ecological systems has become a major topic of concern for the scientific community in the last thirty years. The disaster at Kesterson National Wildlife Refuge in the western San Joaquin River Valley of California, USA has revealed the possible dire effects of a severe build-up of irrigation-induced Se.

Having a similar climate and geology to the San Joaquin River Valley, the Lower Arkansas River Valley (LARV) in southeastern Colorado, USA is a region threatened by high concentrations of Se in both ground and surface water. Colorado State University (CSU), in cooperation with the Colorado Department of Public Health and Environment (CDPHE), began assessing Se, as well as other constituents and in-situ parameters, in a study region downstream of John Martin Reservoir in 2003. After three years of data collection, a study region just upstream of John Martin Reservoir was added in 2006. This effort has resulted in an extensive field data set with 44 sampling events gathering 1949 and 709 ground and surface water Se samples, respectively, as well as 51,927 other water quality measurements. This ongoing collection of data will be used to construct and calibrate regional scale models used to test the effectiveness of proposed best management practices.

Average dissolved Se concentration, C_{Se} , in ground water was found to be 59.9 µg/L and 33.2 µg/L in the Upstream and Downstream Study Regions, respectively, greatly exceeding the current ground water livestock maximum contaminant level (MCL) standard of 20 µg/L. While the chronic standard for C_{Se} in surface water currently is set by both the United States EPA and the CDPHE at 4.6 µg/L (85th percentiles), the 85th percentiles of C_{Se} in surface water samples from the Arkansas River in the Upstream and Downstream Study Regions were 12.6 µg/L and 14.9 µg/L, respectively.

The influence of other constituents, in-situ water quality parameters, and geology upon C_{Se} has been explored and is presented in this thesis. It was found that C_{Se} is strongly and significantly correlated with specific conductivity; uranium, sodium, magnesium, nitrate, sulfate chloride, and boron concentrations; and total dissolved solids in the ground water of both study regions. Distances between monitoring wells and identified underlying marine shale locations along principal ground water flow paths have been estimated. Correlations between these distances and C_{Se} in ground water suggest that, when oxidized by ground water, Se from underlying Cretaceous marine shale deposits is likely to be mobilized and transported into surface water bodies.

Anthropogenic processes may play a key role in this process. Correlations indicate that nitrate is a significant source of the oxygen required in the biochemical process of transforming immobile Se from the forms of seleno-pyrite ($FeSe_2$), elemental Se, or selenite (SeO_3) into the highly soluble form of selenate (SeO_4^{VI}) and inhibiting chemical reduction. Control of the application of irrigation water and nitrogen fertilizer up-gradient of known underlying Se-

bearing formations may become key best management practices for the mitigation of biological Se toxicity.

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Chapter I

INTRODUCTION

1.1 Problem Definition

Selenium (Se) is a naturally occurring element that is essential for the cellular function of a variety of plant and animal life. However, a precarious balance must be maintained. While these organisms only require small quantities for cellular function, high Se concentrations can be toxic. Also, Se bio-accumulates in the food chain which may perpetuate overexposure. Birth deformities, reproductive failure, cirrhosis of the liver, pulmonary edema, and death may result from prolonged Se toxicity (Lemly 2002).

While adverse symptoms were observed in livestock as early as 1275 A.D. by Marco Polo in his travels to western China (Trelease and Beath 1949), the first account in the United States of the toxic effects of Se, referred to then as “alkaline poisoning”, was documented in calvary horses around 1857 by Dr. Madison, physician and veterinarian of Fort Randall in South Dakota. A researcher finally discovered in 1929 that alkaline disease was attributed to forage growing near Niobrara Shale outcrops and containing large quantities of Se (Trelease and Beath 1949). These types of reports are rare because there are few areas in the world in which plants and soil contain toxic levels of Se. It is thought that Se toxicity was the cause of thousands of cattle and horse fatalities in the 1930s and 1940s (Seiler 1999). While tragic, this raised awareness and increased research into Se effects upon livestock.

In 1983 Se toxicity gained the attention of the international scientific community with the Kesterson National Wildlife Refuge disaster in the San Joaquin Valley of California, USA. Dissolved Se draining into the reservoir and evaporation ponds from irrigated land built up to critically high levels (Schuler et al. 1990). These extreme concentrations in the surface waters of the refuge resulted in a bioaccumulation of toxic levels of Se causing deformed waterfowl, aquatic life reproduction problems, and a large fish kill (Presser et al. 1994).

The Kesterson disaster ignited media and political interest in irrigation drainage water quality. As a direct response, the United States Department of the Interior (USDOI) started the National Irrigation Water Quality Program (NIWQP) in 1985. This program evaluated and remediated irrigation drain water impacts to refuges, provided the source of contamination was a USDOI irrigation project (www.usbr.gov/niwqp). One action item of this program was the identification of regions having high Se concentrations or which may be vulnerable to a Se buildup.

The LARV in southeastern Colorado is one region that was designated by the NIWQP as at risk for Se toxicity (Engburg 1990). The LARV, especially west of the John Martin Reservoir, has large quantities of underlying marine shale deposits, known to be a natural Se source. Also, low annual precipitation occurs in conjunction with high potential evapotranspiration (ET). This, coupled with intense agricultural irrigation, promotes Se mobilization, evapoconcentration, and buildup in the soil, ground water, and surface water.

Due to responsibilities under the Endangered Species Act and the Migratory Bird Treaty Act, Federal and State governments need to maintain acceptable water quality and quantity in the waterways of the United States. The federal government, more specifically the United States

Environmental Protection Agency (USEPA) has ultimate authority in regulating water quality standards. While States are required to assign water quality standards, the USEPA has the power to reject State proposed standards. Additionally, each State is required to establish maximum daily loads in waters that will allow the propagation of fish and wildlife and to develop a continuing planning process which is robust enough to accommodate changing pollution patterns (www.epa.gov). Water quality may become impaired by either point or non-point source pollution. Point source pollutants have a single identifiable source where non-point source pollutants derive from many different sources. Although difficult to quantify and manage, non-point sources contribute the vast majority of Se buildup and loading to surface water bodies in the western United States (Presser 1994).

Non-point pollution is difficult to manage for several reasons. First, there may be several sources of the pollutant, some (or all) of which may be unknown to the manager. Often times, the locations of these sources are either only estimated or are entirely unknown. Also, it is difficult to estimate loading rates when multiple sources exist. It is not surprising that a large effort is required when establishing Total Maximum Daily Loads (TMDLs) and determining Best Management Practices (BMPs) for non-point source pollutants.

Lemly (2002) proposed a seven step plan for establishing environmentally safe TMDLs for Se. These steps are as follows: "1) Delineate and characterize the hydrological unit (HU, i.e., water body) of interest. 2) Determine Se concentrations and assess biological hazard. 3) Determine sources, concentrations, and volumes of Se discharges; calculate existing Se load. 4) Estimate retention capacity of HU for Se. 5) Calculate the total allowable Se load and specify reductions needed to meet the target loading. 6) Allocate Se load among discharge sources. 7) Monitor to

determine effectiveness of Se load reduction in meeting environmental quality goals.” Simply stated, detailed research is needed to thoroughly accomplish each of these steps and to produce sound Se TMDL guidelines.

1.2 Research Objectives

The Colorado Water Quality Control Division (CWQCD), a division of the Colorado Department of Public Health and the Environment (CDPHE), monitors, protects, and restores Colorado’s water quality. The CDPHE funded the Civil and Environmental Engineering Department of Colorado State University (CSU) to begin work in April 2003 toward the goal of finding solutions to mitigate Se buildup in the ground and surface waters of the LARV. This effort, initially focused on both Se and iron (Fe) contamination, has adapted over time as results have provided additional insight. The effort has encompassed two previous projects and a third project is currently underway. Named the DATA AND MODELS FOR PLANNING OF NONPOINT SOURCE SELENIUM MANAGEMENT OF THE LOWER ARKANSAS RIVER BASIN, COLORADO, the current project has 11 tasks organized under 3 objectives (Table 1.1).

While every part of the project is crucial to the ultimate goal of protecting aquatic life and water quality, this thesis primarily focuses upon the author’s responsibilities, found under tasks 1, 2, 4, and 5. This work is fundamental to understanding the extent and complexity of the problem of Se buildup in the LARV and must be fully organized, explored, and presented before more advanced tasks, such as building a Se transport model, applying the model to investigate mitigation strategies, or providing recommendations to the CWQCD, may be completed.

Table 1.1. Overview of CSU-CDPHE Se Project Objectives and Tasks (with tasks associated with this thesis shaded grey).

Objective 1: Identify the occurrence, severity, and distribution of Se and its relationship to other constituents and properties in ground water, surface water, and soils of the irrigated stream-aquifer system of the LARV and document the methods and findings.
Task 1: Collect and analyze water samples for Se concentration, U concentration, specific salt concentrations (including nitrate and sulfate), TDS, and related properties [e.g. pH, electrical conductivity (EC) as specific conductance, temperature, oxidation reduction potential (ORP), DO, etc.] and measure water table depth in ground water.
Task 2: Collect and analyze samples for Se concentration, U concentration, specific salt concentrations, TDS, and related properties in surface water.
Task 3: Calculate non-point source Se mass loading rates along the river segments within the study regions using mass balance procedures.
Task 4: Investigate the correspondence of measured Se concentrations and estimated loading rates with average recharge rates from canal seepage, irrigation, and precipitation; with underlying geologic formations; with redox reactions associated with nitrogen fertilization, and with adsorption and related reactions.
Task 5: Estimate correlation and regression relationships of Se concentrations with U concentrations, TDS, specific salt concentrations, and related properties.
Task 6: Determine the redox and adsorption capacity of soils within the Arkansas River Valley region in relation to Se species (particularly selenate and selenite), and create a conceptual model of the fate and transport of Se species dependent on type of surface cover, agricultural practices, and seasonal changes of the temperature and pH of the ground water.
Objective 2: Develop, calibrate, test and apply a model for ground water transport of Se in the study regions and apply to investigate strategies for reducing Se contamination in the LARV and to document the methods and results.
Task 7: Amend the current GMS models (using MODFLOW coupled with RT3D) developed for the Segment 1b and 1c regions to include reactive ground water transport of Se; calibrate model parameters against observed ground water levels, Se concentrations, salt concentrations, ground water return flow rates, and salt and Se loads to the tributaries and river; and test model predictions against observations in an independent subset of the data.
Task 8: Apply the model to simulate Se concentrations and loading to the river in Segments 1b and 1c (and to the extent possible, Segment 1a) under improved management strategies, including increased irrigation efficiency, reduced canal seepage, leasing/rotational fallowing, and managed application of nitrogen fertilizers.
Objective 3: Manage and report on the project implementation.
Task 9: Ensure that project objectives and tasks are being accomplished within the estimated schedule; ensure compliance with the general procedures and protocol described in the project implementation plan and the sampling and analysis plan; and ensure that project costs are kept within the specified budgetary guidelines.
Task 10: Participate in periodic meetings (including conferences and workshops) with CWQCD personnel, cooperators, stakeholders, and the general public to disseminate information and obtain feedback related to this project; provide technical assistance to project collaborators, as needed; and publicize findings through newspaper articles and the project website.
Task 11: Prepare and submit semi-annual written reports and a final written report summarizing project methods, findings, and recommendations to the CWQCD within the prescribed schedule.

Chapter II

LITERATURE REVIEW

2.1 Irrigation-Induced Effects on Soil and Water Quality

Since the beginning of agriculture, tools and methods have been developed to increase crop yield. The practice of irrigation was one of the first of these. Irrigation became widely known in Mesopotamia, the Nile Valley in Egypt, the Khusistan area of Iran, and the Indus Valley of Pakistan around 3500 B.C. (Nace 1972). Without irrigation, widespread agricultural production would not be possible in several areas of United States, such as the Arkansas River Basin in Colorado and Kansas and the Imperial Valley in Southern California. Most irrigation projects in the United States are between 75 and 150 years old, due to a surge of irrigation projects constructed in the early twentieth century.

Irrigation is used extensively throughout the world, accounting for approximately one third of global food production (Ghassemi et al. 1995) and requiring about 90% of the world's fresh water use (Scanlon et al. 2007). In 2008, the United States applied about 112,600 million m³ (91.2 million acre feet) of water on 222,200 km² (54.9 million acres) of irrigated land. Approximately 59,820 million m³ (48.5 million acre-feet) of irrigation water was supplied from ground water while 52,790 million m³ (42.8 million acre-ft) was diverted from surface water sources (www.agcensus.usda.gov). Reliance upon irrigation varies greatly depending on region.

States east of the Mississippi River tend to receive ample rainfall and generally do not use as much irrigation as western states. In 2002 California withdrew the most water for irrigation (22% of the total 137,000 m³/day withdrawn for irrigation in the US in 2000), followed by Idaho withdrawing 11%, then Colorado withdrawing 8% (www.usgs.gov). Irrigation plays a major role in producing Colorado's \$2.0 billion crop economy. About 1.16 million ha (2.87 million acres) of Colorado's 2.38 million ha (5.89 million acres) of total harvested cropland were irrigated in 2007 (www.agcensus.usda.gov).

While irrigation is crucial in meeting current agricultural demands, the practice of applying ground or surface water upon cropland over extended periods of time usually results in problems such as salinization (an increase in total dissolved solids (TDS) in water and soil) and waterlogging. These adverse conditions reduce crop yields and, if left unchecked, may result in an associated ecologically toxic buildup of salts and other minerals.

Salinization may be derived from both natural and anthropogenic processes, respectively referred to as primary and secondary salinization. Processes occurring over very long periods of time, such as erosion and dissolution of saline geological formations and deposition of saline material and solution into downstream areas or by recession of prehistoric seas, are causes of primary salinization. Secondary salinization is caused by human activities, such as irrigation, over relatively short periods of time (Ghassemi et al 1995). By definition, irrigation alters a region's surface and ground water hydrology by increasing water contents of soils otherwise too dry to produce optimum crop yields. The water applied in agricultural irrigation is never as pure as rainwater, containing a variety of salts and other ions. Crops typically absorb few dissolved ions as they extract water from the soil; therefore, the majority of these dissolved solids are left

behind in the soil. If not properly managed, a build up of these salts over time may result in severe crop yield reductions and eventually render the soil unfertile.

During irrigation, excess water is often applied in an effort to completely refill the crop root zone. This surplus water either runs off the field surface and is collected in drainage ditches or percolates below the root zone into existing ground water. If the existing drainage structure is insufficient, a region's water table elevation may rise and intrude upon the crop root zone. This causes waterlogging, a condition of too much water and too little air in the soil pores of the root zone for ideal crop growth. Saline high water tables also may contribute to increased salinization of overlying soils through the process of evapoconcentration, in which ground water near the ground surface evaporates, leaving behind salts and minerals in the root zone. Salts also may be dissolved from underlying sediments and rocks further increasing salinity.

While salinization is the most widely known adverse effect of irrigation, accumulation of other impurities in the soil, ground water, and surface water bodies may also have harsh consequences. An extreme example of this would be the Se buildup caused by dissolution and evapoconcentration of irrigation return flows in the San Joaquin Valley of California, USA. Kesterson Reservoir was a terminal evaporation and water storage facility accepting the drainage from approximately 100 km (Weres et al. 1990) of central California's irrigated farmland. Dissolved Se, thought to have originated in underlying marine shales and mobilized by irrigation (Presser 1994, Deverel 1988), draining into the 12 evaporation ponds, totaling 5 km², built up and reached critically high levels in 1983, causing deformed waterfowl, aquatic life reproduction problems, and a large fish kill (Deverel 1988). Samples taken from the reservoir and drain revealed Se concentrations as high as 350 and 1400 µg/L, respectively, resulting in

Kesterson NWR being labeled as a toxic waste dump in 1987 (Presser 1994, Wright 1999). The reservoir has since been drained and partially buried.

The Kesterson disaster has taught water resource managers the importance of monitoring and managing Se concentrations in areas susceptible to toxicity. While great advances have been made through the extensive research following this ecological tragedy, several areas of the United States (e.g. Lower Arkansas River Basin, CO and the Solomon River Basin, KS) and world (e.g. Soan-Sakesar Valley, Pakistan and the Daba Mountain Area, China) continue to exhibit rising concentrations of Se in surface and ground water.

2.2 Selenium Chemistry and Characteristics

The element Se was discovered as a byproduct of sulfuric acid production by Jons Jakob Berzelius in 1817. A transitional element located in the oxygen group and having properties of both metals and non-metals, Se has an atomic number of 34 and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$ (Encyclopedia Britannica 2010). Having a similar valence structure as sulfur (S), Se does not have any natural radioactive isotopes and naturally occurs in four oxidation states: selenide (Se^{2-}), elemental Se (Se^{0+}), selenite (Se^{4+}), and selenate (Se^{6+}), as well as several organic compounds (Masscheleyn 1989). Since these oxidation states have differing mobility characteristics, oxidation-reduction (redox) reactions primarily control the dissolution, sorption, and mobility of Se (Masscheleyn et al. 1989, Jayaweera and Biggar 1996). This being the case, pH and EH, a measurement of the chemical electrons in a system (Benjamin 2002), may be used to estimate Se behavior. Masscheleyn et al. (1989) studied how pH and EH affected Se solubility, speciation, and volatilization. They found that above EH = 200 mV selenite (SeO_3) slowly oxidized into the soluble form of selenate (SeO_4). They also reported that above

$\text{EH} = 450 \text{ mV}$, pH plays a role in Se speciation with selenate comprising 95% of total soluble Se at high pH values (8.9,9) and comprising only 75% of total soluble Se at low pH values (6.5,7.5). Jayaweera and Biggar (1996) found similar results with EH being directly related to the amount of selenate. Additionally, they reported that wetting and drying of seleniferous soils, such as in the case of irrigation, results in oxic and anoxic cycles causing cyclical variations in the concentration of soluble Se in the environment.

Selenide is the most reduced form of Se and is usually found in the form of metal (Fe, Cu, or Pb) selenides, organic selenide, or hydrogen selenide (McNeal and Balistrieri 1989). Because the selenide ion (Se^{2-}) has similar ionic radii to the sulfate ion (S^{2-}) Se is an isomorphic substitute for S (Presser 2004). While the strong adsorption properties of selenide provide immobility, it is possible that selenide may be slowly oxidized over time becoming a primary source of Se contamination. Also, microbial processes as well as plants may volatilize selenide into poisonous gas in the form of hydrogen selenide (Terry et al. 1992), although this is usually quickly oxidized into elemental Se (Sarquis and Mickey 1980).

In general, elemental Se (Se^{0+}) acts as an environmentally stable, immobile sink for Se. Se^{0+} is very insoluble and usually remains as such with slow oxidation or reduction kinetics (Sarquis and Mickey 1980). Elemental Se is the form primarily used in the glass manufacturing, chemical, and pigment industries. Its grey hexagonal crystals exhibit electronic and photoelectric properties.

Selenite (Se^{4+}) is the next oxidation state after elemental Se (Presser 1994). Selenite is slightly more soluble than elemental Se; however, it is highly sorptive, especially in the presence of iron or aluminum minerals (Sarquis and Mickey 1980). This sorption is controlled by pH, particle

concentration and composition of the medium, selenite concentration, and competition of competing anions such as phosphate. Its high sorptivity causes selenite to resist biological accumulation; hence, selenite does not largely contribute to Se contamination. Selenite is rapidly reduced to elemental Se in the present of mildly reducing agents such as ascorbic acid and sulfur dioxide. Additionally, in the present of ferric oxides and aluminum oxides in an aqueous environment, most selenites reduce to elemental Se (Sarquis and Mickey 1980).

Selenate (Se^{6+}) is the highest oxidation state for Se. Careful monitoring and management of selenate is needed in susceptible areas because this form of Se contributes the most to Se toxicity. In most cases, selenate composes the majority of dissolved Se found in the environment. Although strongly controlled by redox conditions of the soil, selenate is the most soluble of the Se forms making it highly mobile. Due to its high mobility selenate is highly available for bioaccumulation by plants and aquatic life (Sarquis and Mickey 1980). It also has been found that Se is in thermodynamic equilibrium as selenate in highly oxidized and alkaline environments, such as alkaline weathered rocks in arid climates and in alkaline irrigated soils. In summary, selenate is the most dangerous form of Se found in the environment (NAS-NRC 1972, Sarquis and Mickey 1980).

2.3 Effects of Selenium on Aquatic Life

There have been several studies researching how high Se concentrations in water can cause damage to aquatic life. Also, otherwise safe concentrations of Se may reach toxic levels through bioaccumulation in the food chain (Lemly 2002).

Lemly (2002) conducted an excellent study of long-term effects of Se toxicity upon twenty species of fish in Belews Lake, NC. Effects upon species include 1) gill lamellae swelling; 2) lymphocyte elevation; 3) anemia; 4) corneal cataracts; 5) pop-eye; 6) pathological alterations in the liver, kidney, ovaries, and heart; 7) reproductive failure; and 8) teratogenic deformities of the head, spine, mouth, and fins. Death may occur if egg tissue concentrations are high ($10 \mu\text{g/g}$ or greater).

Debruyn and Chapman (2007) investigated the effects of Se on 29 macroinvertebrate species. They found that sub-lethal effects on invertebrates began occurring at 10-fold lower concentrations than lethal concentrations. It was concluded that some invertebrate species experienced toxic effects at Se concentrations considered safe for organisms higher on the food chain.

High Se concentrations also can affect aquatic birds. For example, at the Kesterson Reservoir low reproductive success, high mortality, and developmental abnormalities were seen in embryos and chicks (Schuler et al. 1990). These effects resulted from extremely high Se concentrations in bird tissues and eggs. Aquatic bird livers from a nearby area (Volta Wildlife Management Area) contained Se concentrations between 4 and $9 \mu\text{g/g}$ while livers from Kesterson ranged between 20 to $127 \mu\text{g/g}$ (dry weight). H.M. Ohlendorf has published several papers studying the effects of Se on avian life in the Kesterson Reservoir. He reported factors influencing bird tissue Se concentrations included length of residence, consistency of feeding within Kesterson Reservoir, and Se concentration in food chain biota (Ohlendorf et al. 1990).

2.4 Sources and Historical Occurrence of Selenium

Non-point source Se loading to water bodies originates from a variety of sources. The discovery that Se in pasturage was causing horse and cattle fatalities prompted a major study of the sources and occurrences of Se in the western United States in the 1930's and 1940's. As early as 1941 researchers were suspecting "soils derived from materials of the Cretaceous Age" as primary Se sources (Lakin and Byers 1941).

The primary economic source of Se is as a byproduct of sulfide ore processing. It is not mined as a primary metal anywhere in the world as it does not concentrate in the earth's crust to form any economical deposits (Cota 2005). Anthropogenic sources include, but are not limited to, coal mining and combustion; gold, silver, nickel, and phosphate mining; metal smelting; municipal landfills; oil transport, refining, and utilization; constructed wetlands; and disposal of flyash and feedlot wastes. However, in the semi-arid or arid irrigated regions in the western United States underlying Cretaceous Age marine shale likely is the key culprit of catastrophic Se accumulation.

While rarely found in its elemental form, Se may be abundant in areas containing marine shale deposits. Se partially replaces sulfur in sulfide ores, such as pyrites found in such shales. Presser (1994) outlines what she has named the "Kesterson Effect". The following is her detailed "history" of Se, and while written in reference to the San Joaquin Valley in California in response to the Kesterson National Wildlife Refuge disaster, it generally applies to the process that is occurring in the Lower Arkansas River Basin in southeastern Colorado as well as to other semi-arid or arid irrigated areas throughout the world containing marine shale deposits.

1. During the Cretaceous Period and the Eocene and Miocene epochs Se was enriched in ancient seas by either the
 - a. Deposition or washing in of volcanic eruptive material, or
 - b. Biogenic accumulation from seawater into the food chain at sites of nutrient-rich continental slope upwellings.
2. Either "abiotically" or "biotically," Se was substituted for S in sulfides formed during digenesis of sediments, ultimately resulting in high concentrations of Se in pyritic marine shales.
3. The exposure of seleniferous sedimentary rocks is caused by the seas retreating and the Coast Ranges shales being uplifted during the Tertiary Period.
4. These source shales are rapidly weathered in an arid climate, which produces unstable, steeply dipping slopes mostly devoid of vegetation.
5. Extensive alluvial fan areas are developed by mass wasting, in the form of mud and debris flows, delivering high volumes of sediments into fast flowing streams of short duration.
6. Particulate reduced and intermediate oxidation states of Se are transported to the valley, which results in the constant renewing of a low-level background concentration of Se in soils.
7. Acid is produced and Se released during the oxidation of pyrite caused by the further weathering of the shales in the Coast Ranges generating briny, seleniferous, sulfate seeps of pH 4 found indicative of source shales.
8. Fractional crystallization of sulfate minerals, caused by neutralization by introduction into an alkaline carbonate environment and the evaporative concentration of these

waters, yields soluble selenate incorporated in hydrous sodium and magnesium sulfate salts.

9. Water movement from the capillary fringe through many evaporation-dissolution cycles on summit slopes causes concentration of these salts, creating salt crusts and from downgradient subsurface flow on toeslopes, salt-layering.
10. A main mechanism of transport of Se is facilitated by the salts being extensively mobilized in both solid and aqueous phases. Mobilization occurs by
 - a. mass wasting of salts which generates high concentrations of Se in recent debris and mud flows; and
 - b. solubilization of salts in the regional watershed which generates high concentrations in runoff and throughflow from the flushing events of winter.
11. Additional selenate salts on farmland soils are provided by oxidation of particulate Se transported from above and promoted by alkaline soil surfaces on the valley floor. Irrigation leaches the salts, including Se, into the existing shallow ground water aquifer.

Although other publications echo parts of this story (i.e. Wu 2004, Tidball et al. 1991, and Cota 2005), Presser's (1994) report provides the most complete description of Se "history". Presser (1994) also states that "The extensive areal development in the western United States of the Cretaceous Western Interior Seaway and its downwind relationship to volcanic fields in the Rocky Mountain region provided a greater opportunity for volcanic Se deposition in marine sediments than in California".

2.5 Relationships between Selenium and Various Constituents

Following the Se accumulation at Kesterson Reservoir in 1981, several attempts have been made to better describe how Se is transported in the environment. A large portion of this effort has been to attempt to find correlations between Se and various other constituents through data acquisition from field and lab sources.

It is not surprising that dissolved Se has been found significantly correlated to dissolved sulfate (SO_4) in several studies. Afzul (2000) and Presser (1994) report significant strong correlations of $r=0.64$ and $r=0.93$, respectively, while Tracy et al. (1990) reports that a highly significant ($p < 0.001$) correlation was found between total dissolved Se and dissolved SO_4 . The strong relationship between Se and SO_4 is most likely due to two reasons. As stated previously, Se and S are very similar elements. They are in the same column of the periodic chart of elements and have a similar valence structure. Having a similar valence structure makes possible the second reason. Research shows that both constituents have the same source material in the environment. Pyrites found in Cretaceous age shales usually are composed of FeS_2 ; however, in some cases Se is able to replace S resulting in FeSe_2 (Presser 1994).

Highly reduced forms of Se and S found in pyrite may be oxidized into more mobile forms through redox reactions. Sposito (1991) reports that mobility and solubility of Se in the soils of the western San Joaquin Valley in California can be controlled by oxidation-reduction reactions. Since these redox reactions are highly related to microbial content, it is not surprising that organic carbon has been found to have a significant positive correlation with total Se in agricultural soils (Yamada 2009). Martens et al. (1997) reports that Se would be expected to increase with increased carbon oxidation and Weret et al. (1990) found that, while drying a soil

drastically lower its likelihood of reducing selenate, this effect is readily reversible by adding organic carbon.

The pH of a soil, another property highly related to microbial content, also was found to be correlated with concentrations of Se. Masscheleyn (1989) reported that the highest total dissolved Se concentrations were found at pH = 6.5 and that selenite adsorption decreases with increasing pH over a range of 4 to 9. Afzul (2000) found selenate and pH to be linearly correlated in both ground and surface water in the Soan-Sakesar Valley, Pakistan and states that water containing higher pH values (7.2-7.9) may contain a higher percentage of total Se in the form of selenate.

Perhaps the most important correlation found is between Se and NO₃. Large amounts of N fertilizer are applied to irrigated agricultural regions. If dissolved Se is found to be directly related to NO₃, then regulating the application of agricultural fertilizer may result in effective best management practices for Se control. Sposito (1991) reports that chemical thermodynamics predict that, at pH greater than five, NO₃ should be reduced first, followed by selenate, followed by manganese oxide. It also was shown that retardation of selenate reduction occurred in the present of added NO₃ (Sposito 1991). Weres et al. (1990) researched the effects of NO₃ upon Se mobility and concluded that, while removal of selenite from water is an inorganic process unaffected by NO₃, removal of selenate from water was governed by microbial processes and significantly inhibited by NO₃. Also, NO₃ was found to significantly lower the likelihood of selenate's reduction in pond sediment and that complete removal of NO₃ is required before reaching total selenate removal (Weres et al. 1990).

Se also has been found to be correlated with boron (B) and uranium (U). Hudak (2004) reported that in Texas, USA several wells with high B concentrations also produced high Se concentrations and a statistically significant ($\alpha = 0.05$) Spearman correlation between these constituents was calculated as 0.58. It was hypothesized that irrigation return flows and oil field brine contributed to high concentrations of Se and B.

Zielinski et al. (1995) found Se to be strongly and significantly ($\alpha = 0.05$) correlated with U ($r = 0.79$) in the LARV. This study also found an extremely high and statistically significant ($\alpha = 0.05$) correlation between U and B with $r = 0.96$. It is thought that U is mobilized by the same processes as Se. U concentrations are thought to be increased by the weathering of U-bearing Cretaceous Age source shales and high rates of evapoconcentration related to the semi-arid climate and typically high water tables (Zielinski 1995).

As discussed, several studies have found Se to be correlated with various constituents. Although most of these correlations are founded upon a limited data set, they do indicate that the mobilization and transport of Se is a fairly complex process involving primary sources, such as Cretaceous shales or anthropogenic pathways, ground and surface water flow rates, and redox reactions involving pH and microbial agents, as well as concentrations of competing ions. Proper integration of these many factors will lead to the most effective Se management models.

2.6 Selenium Volatilization

Plant and soil volatilization may be a sink for Se. Zieve and Peterson (1981) found that the rate of Se volatilization from soil was dependent upon concentration of water soluble Se, moisture, temperature, time, microbial activity, and season. Karlson and Frankenberger (1989) studied

possible Se volatilization acceleration techniques using active carbon traps in Californian soils. They found that without adding carbon, the volatilization rate of selenite was an order of magnitude higher than selenate's volatilization rate. However, the addition of carbon into the soil was found to accelerate selenate's volatilization rate to that of selenite. Banuelos (2005) found that Se volatilization rates in the drainage sediment from the San Luis Drain in Central California were found to be relatively low due to high sulfate levels. Recently, D.O. Whittemore of the Kansas Geological Survey conjectured that volatilization from the John Martin Reservoir may be a significant Se sink (Whittemore 2009).

Chapter III

DESCRIPTION AND RESEARCH HISTORY OF STUDY SITES

3.1 Nature and Characteristics of the Study Sites

The Arkansas River Basin is the largest in Colorado, covering approximately 73,260 square kilometers (28,286 square miles). Starting at Mount Elbert, Colorado's highest peak at 4,399 meters (14,443 feet), and stretching all the way to Colorado's lowest point of 1,021 meters (3,350 feet), the Arkansas River Basin is bordered by the continental divide in the west, the New Mexico state line in the south, and the Kansas state line in the east (Encyclopedia Britannica 2010). In addition to its primary uses in providing drinking water for the Front Range and irrigation water for the eastern plains, the Arkansas River is the most recreated river in Colorado. Figure 3.1 shows the Arkansas River Basin drainage within Colorado, including the Lower Arkansas River Valley (LARV). Colorado's LARV comprises the land above the Arkansas River alluvium, bordered by Pueblo on the west and the Colorado-Kansas state line on the east.

The LARV has a semi-arid climate with an average annual precipitation of about 0.37 m (14.6 inches) and an average potential evaporation of approximately 1.47 m (58 inches). Several stations record flow parameters along the Arkansas River in Colorado with the USGS gauging station 7133000 located at Lamar, CO having recorded data as far back as 1913. This station recorded a maximum annual flow rate of $44.1 \text{ m}^3/\text{s}$ (1557 cfs) in 1942, a minimum average flow

rate of $0.3 \text{ m}^3/\text{s}$ (11.1 cfs) in 1939, and an average flow $5.2 \text{ m}^3/\text{s}$ (185 cfs) of over the period between of 1913-2009 (www.waterdata.usgs.gov).

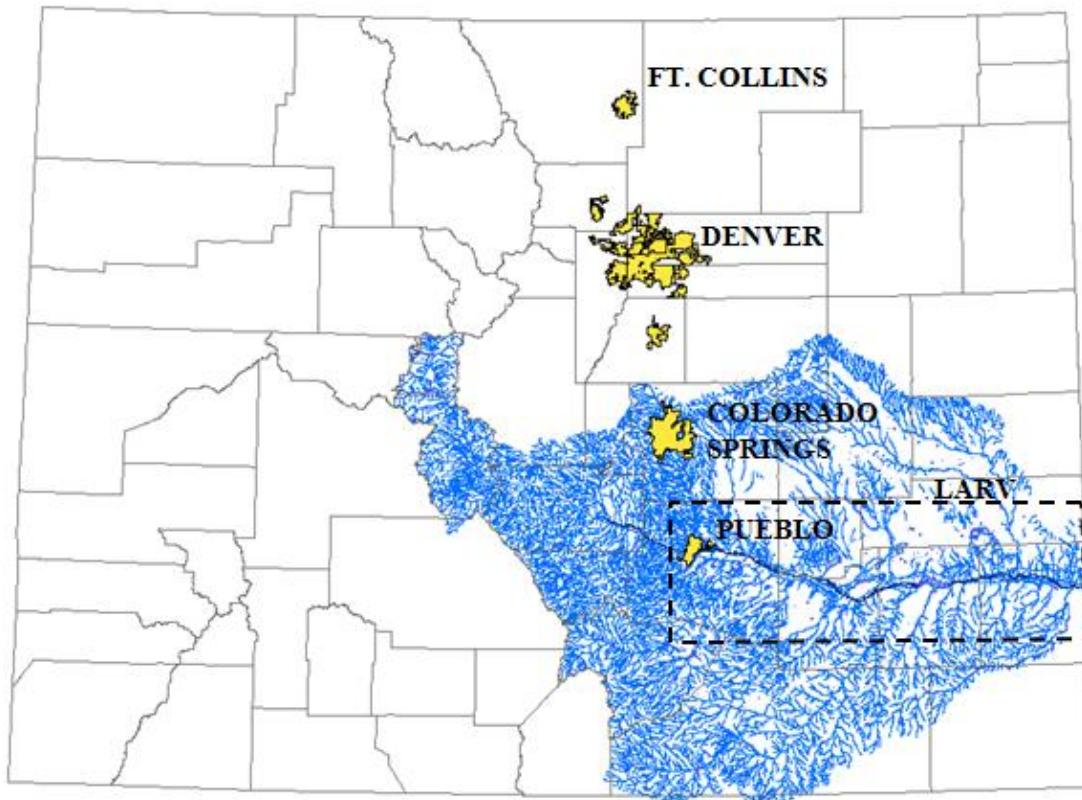


Figure 3.1. The Arkansas River Basin within Colorado with the LARV highlighted

Figure 3.2 shows all USGS gauging stations in the LARV that have recorded streamflow and/or specific conductance (EC standardized at 25°C) while Table 3.1 provides statistics with respect to these stations. The maximum and minimum values show that there is a large amount of streamflow variability in the Arkansas River. Figures 3.3 and 3.4 plot mean daily flow rates in the Arkansas River from January 1, 1996 to September 30, 2007 for USGS Stations 07119700 and 07133000, respectively. Specific conductance statistics are also displayed in Table 3.1 showing an increasing downstream trend in the Arkansas River (www.waterdata.usgs.gov).

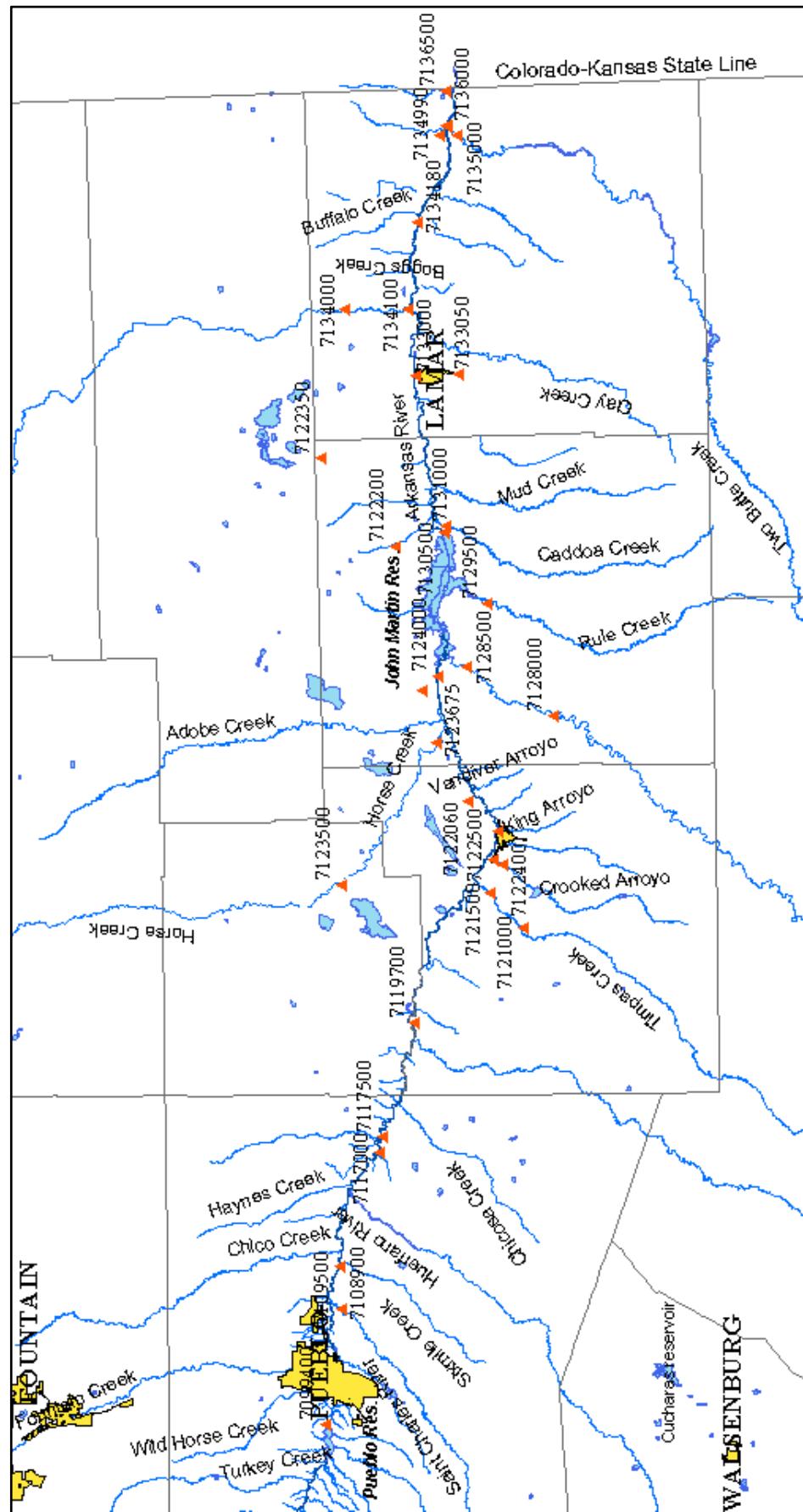


Figure 3.2. Selected USGS Gauging Stations within the Lower Arkansas River Valley

Table 3.1. USGS Gauging Stations in the LARV Monitoring Streamflow and/or Specific Conductance

USGS Station ID	Description	Latitude	Longitude	Streamflow (m ³ /s)				Specific Conductance (dS/m)					
				Start Date	End Date	Max	Min	Avg.	Start Date	End Date	Max	Min	Avg.
07093400	ARKANSAS RIVER ABOVE PUEBLO, CO	38°16'18"	104°43'03"	10/1/1965	9/30/2007	167.5	0.01	18.76	4/1/1986	2/28/2010	1.440	0.224	0.480
07108900	ST. CHARLES RIVER AT VINELAND, CO.	38°14'44"	104°29'09"	10/1/1978	2/28/2010	89.3	0.01	1.09	-	-	-	-	-
07109500	ARKANSAS RIVER NEAR AVOIDALE, CO.	38°14'53"	104°23'55"	5/1/1939	1/18/1944	342.9	1.42	26.52	-	-	-	-	-
07117000	ARKANSAS RIVER NEAR NEPESTA, CO.	38°11'03"	104°10'22"	10/1/1935	5/18/1941	405.2	0.34	14.82	-	-	-	-	-
07117500	ARKANSAS RIVER AT NEPESTA, CO.	38°10'44"	104°08'19"	1/1/1914	5/31/1936	279.7	0.00	17.64	-	-	-	-	-
07119700	ARKANSAS RIVER AT CATLIN DAM, NEAR FOWLER, CO.	38°07'33"	103°54'41"	10/1/1964	9/30/2007	518.6	0.00	19.96	5/9/1990	2/28/2010	4.110	0.365	1.072
07121000	TIMPAS CREEK NEAR ROCKY FORD, CO.	37°57'10"	103°43'26"	10/1/1923	9/30/1949	43.4	0.00	1.38	-	-	-	-	-
07121500	TIMPAS CREEK AT MOUTH NEAR SWINK, CO.	38°00'11"	103°39'20"	1/1/1922	2/28/2010	75.7	0.09	1.75	-	-	-	-	-
07122060	FORT LYON CANAL NEAR CASA, CO	38°02'08"	102°28'18"	5/25/1988	11/27/1990	27.7	0.00	6.73	-	-	-	-	-
07122105	FORT LYON CANAL NEAR CORNELIA, CO	38°06'25"	103°14'55"	5/26/1988	11/20/1990	26.5	0.00	7.40	-	-	-	-	-
07122200	FORT LYON CANAL NEAR HASTY, CO.	38°08'39"	102°57'30"	10/1/1968	11/28/1990	27.5	0.00	5.65	-	-	-	-	-
07122350	FORT LYON CANAL NEAR BIG BEND, CO	38°15'29"	102°46'42"	5/26/1988	11/20/1990	15.9	0.00	2.91	-	-	-	-	-
07122400	CROOKED ARROYO NEAR SWINK, CO.	37°58'56"	103°35'52"	2/1/1968	9/30/1993	10.0	0.00	0.33	-	-	-	-	-
07122500	CROOKED ARROYO NEAR LA JUNTA, CO.	37°59'55"	103°35'13"	1/1/1922	9/30/1925	17.1	0.00	0.45	-	-	-	-	-
07123000	ARKANSAS RIVER AT LA JUNTA, CO	37°59'26"	103°31'55"	4/1/1912	9/30/2007	1,731	0.00	7.12	-	-	-	-	-
07123500	HORSE CREEK NEAR SUGAR CITY, CO.	36°14'21"	103°38'04"	4/13/1940	9/30/1947	49.6	0.00	0.21	-	-	-	-	-
07123675	HORSE CREEK NEAR LAS ANIMAS, CO	36°05'06"	103°21'12"	10/1/1979	9/30/1993	16.6	0.00	0.37	10/1/1989	9/30/1993	5.680	1.990	3.865
07124000	ARKANSAS RIVER AT LAS ANIMAS, CO.	38°04'51"	103°13'09"	6/1/1939	2/28/2010	731.1	0.03	6.59	12/4/1985	2/28/2010	7.380	0.631	2.395
07128000	PURGATOIRE R AT HIGHLAND DAM, NR LAS ANIMAS, CO.	37°53'57"	103°18'11"	10/1/1931	9/30/1955	1,295	0.00	3.22	-	-	-	-	-
07128500	PURGATOIRE RIVER NEAR LAS ANIMAS, CO.	38°02'02"	103°12'00"	1/1/1922	2/28/2010	1,312	0.00	2.55	10/1/1989	9/30/1996	5.440	0.412	3.250
07129500	RULE CREEK NEAR CADDOWA, CO.	37°59'58"	103°04'36"	10/1/1941	9/30/1946	14.7	0.00	0.05	-	-	-	-	-
07130500	ARKANSAS RIVER BELOW JOHN MARTIN RESERVOIR, CO.	38°03'59"	102°55'55"	4/1/1938	2/28/2010	946.5	0.00	8.84	12/5/1985	2/28/2010	3.520	0.838	2.109
07131000	CADDOWA CREEK AT CADDOWA, CO.	38°03'46"	102°55'05"	10/1/1941	9/30/1946	10.9	0.00	0.04	-	-	-	-	-
07133000	ARKANSAS RIVER AT LAMAR, CO.	38°06'21"	102°37'05"	6/1/1913	2/28/2010	2,474	0.00	5.06	-	-	-	-	-
07133050	WILLOW CREEK NEAR LAMAR, CO.	38°02'16"	102°36'51"	4/24/1974	9/30/1977	5.84	0.00	0.02	-	-	-	-	-
07134000	BIG SANDY CR ABV AMITY CNL DIVERSN, NR KORNMAN, CO	38°12'52"	102°28'47"	10/1/1941	12/31/1946	58.4	0.00	0.37	-	-	-	-	-
07134100	BIG SANDY CREEK NEAR LAMAR, CO.	38°06'51"	102°29'00"	2/1/1968	2/28/2010	41.4	0.00	0.42	-	-	-	-	-
07134180	ARKANSAS RIVER NEAR GRANADA, CO.	38°05'44"	102°18'37"	12/5/1980	2/28/2010	115.3	0.04	5.06	-	-	-	-	-
07134990	WILD HORSE CREEK ABOVE HOLLY, CO.	38°03'25.30"	102°08'18.50"	6/30/1995	12/1/2009	14.1	0.00	0.56	-	-	-	-	-
07135000	TWO BUTTE CREEK NEAR HOLLY, CO.	38°01'40"	102°08'19"	5/1/1942	9/30/1999	13.3	0.00	0.03	-	-	-	-	-
07135500	ARKANSAS RIVER AT HOLLY, CO.	38°02'37"	102°07'09"	4/1/1910	9/30/1953	1,644	0.00	9.41	-	-	-	-	-
07136000	WILD HORSE CREEK AT HOLLY, CO.	38°02'45"	102°07'05"	10/1/1922	10/31/1950	45.1	0.00	0.41	-	-	-	-	-
07136500	HOLLY DRAIN NEAR HOLLY, CO.	38°02'43"	102°02'53"	1/1/1924	9/30/1950	28.1	0.01	0.92	-	-	-	-	-

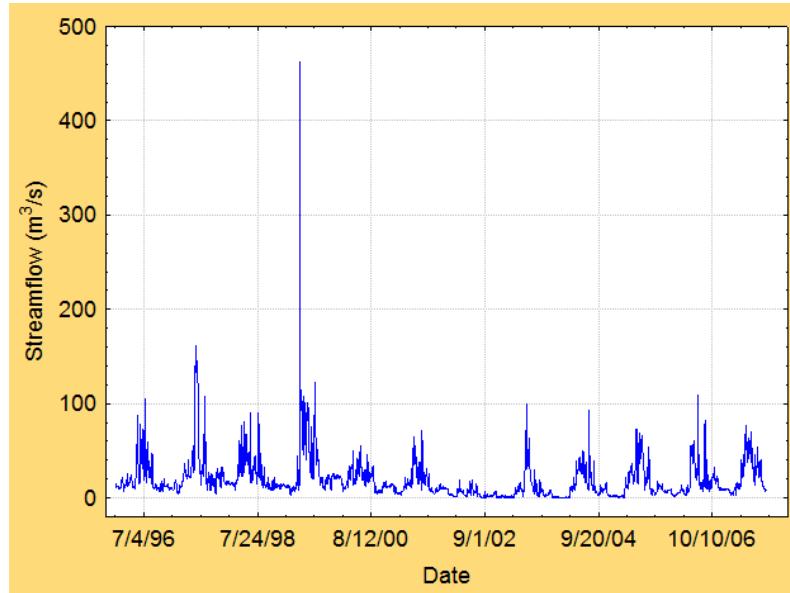


Figure 3.3. Streamflow Data for USGS Gauging Station
07119700 - Arkansas River at Catlin Dam near Fowler, CO

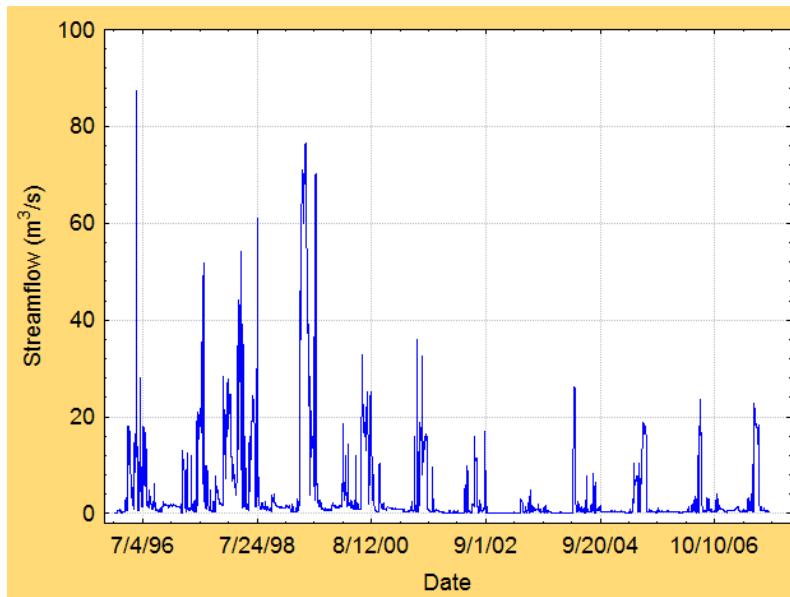


Figure 3.4. Streamflow Data for USGS Gauging Station
07133000 - Arkansas River near Lamar, CO

Having rich soils but a semi arid climate, it is no surprise that irrigated agriculture is the keystone to the economy of the LARV. As stated by Mueller (1991), settlement of this area followed the usual frontier pattern of explorers, trappers, traders, herdsmen, and then, finally, permanent agricultural farmers. This region had a large boost in the number and size of farms during the

gold rush of the late 1850's, starting the era of intense irrigated agriculture in the Arkansas River Valley. Large scale irrigation began in the region at Rocky Ford around 1884 and major appropriations were developed between 1880 and 1910 (Sherow 1990).

There are two major on-stream reservoirs located in the LARV. The Pueblo Reservoir is located on the west side of the city of Pueblo, CO. Completed in 1975, it has a capacity of approximately 440 million m³ (357,000 acre-ft). The older but larger John Martin Reservoir is located just to the east of the town of Las Animas, CO. This reservoir was completed in 1948 and has a capacity of about 762 million m³ (618,600 acre-ft).

Soils of the LARV originate from Eolian sediment, comprised of about one-third sand and two-thirds loess (Madole 1995), as well as decomposed underlying marine sedimentary rocks. The upper soils, about 2 to 3 meters from ground surface, consist of mostly clay-loam surface layers and clay to silt loam sublayers. The shallow alluvial aquifer resides below the upper soils and consists of mostly sand and gravels. This results in relatively high hydraulic conductivities, ranging between 2.46×10^{-3} and 373 m/day (Voegeli 1963). The shallow aquifer reaches depths of up to 60 m. Bedrock, composed of mostly of shale, is located below the shallow aquifer. Several different shale types are prominent in the LARV. From oldest to youngest these include Graneros shale, Greenhorn shale, Carlisle formations, and Niobrara formations (Voegeli and Hershey 1965). While alluvium is the primary geology type within 2 km of the Arkansas River, slopewash material, mostly consisting of sandy silt containing weathered shale and limestone, makes up the upper soil layers beyond the 2 km. However, these descriptions of soil type are general, as the geology in this region is complex and heterogeneous. USGS geological maps of

the region displaying detailed soil type descriptions and locations may be found in Sharps (1976), Scott (1968), and Scott et al. (1978).

Over the last century Colorado and Kansas have had continual legal disputes regarding use of the waters of the Arkansas River. Kansas first sued Colorado for excessive use back in 1907 (*Kansas v. Colorado*, 206 U.S. 46). The Arkansas River Compact was ratified by Congress in 1949 after three years of negotiations between Colorado and Kansas. The compact states in Article IV-D that “The compact is not intended to impede or prevent future beneficial development of the Arkansas River provided that the development does not ‘materially deplete’ state line flows in ‘usable quantity of availability for use.’” Kansas sued Colorado again in 1985 claiming that ground water mining, or the removal and consumption of alluvial ground water, in Colorado had violated the compact. The case went before the U.S. Supreme Court in 1995 and it was ruled that the compact had been violated due to post-compact ground water use “materially depleting” the usable flow at the Colorado-Kansas state line (*Kansas v. Colorado*, 514 U.S. 673). In 2004 the U.S. Supreme Court ruled that Colorado had over-used more than 490 million m³ and ordered Colorado to pay Kansas \$38 million in restitution (*Kansas v. Colorado*, 125 S. Ct. 526).

The LARV is one of Colorado’s most productive agricultural areas. Major crops grown in this region include alfalfa, corn, wheat, grass, onion, sorghum, cantaloupe, and watermelon (Burkhalter and Gates 2005). The most common irrigation techniques used are border irrigation and furrow irrigation. Unfortunately, several water management problems have developed due to intense irrigation over the last century. Salinization, waterlogging, water lost to non-beneficial use, and non-point source loading of salts and minerals have all affected the productivity and ecology of the region (Burkhalter and Gates 2006).

3.2 Previous State and Federal Water Quality Research in the Arkansas River Valley

Several relevant studies regarding the water quality in the LARV have been conducted in the past by various State and Federal agencies. The majority of these have focused on irrigation-induced water and soil problems and only a few have studied Se to any significant degree. In addition to the following discussed studies there is ongoing unpublished research by the Kansas Geological Survey on Se volatilization in the LARV. Results from these studies may indicate that a significant amount of Se is volatilized from the John Martin Reservoir.

3.2.1 STORET and WQCD Water Quality Monitoring

The WQCD of the CDPHE has been collecting water samples for the analysis of Se concentration, C_{Se} , since about 1968 and stores such data on STORET, an online database developed by the United States Environmental Protection Agency (USEPA) to share water quality, physical, and biological data (<http://www.epa.gov/storet/>). A search of this database returned 1150 sample results for dissolved C_{Se} and 1260 results for total C_{Se} in the LARV. These samples varied greatly both spatially and temporally therefore resulting in a varied dataset giving inconsistent statistics (Table 3.2).

Table 3.2. STORET Data Summary for C_{Se} ($\mu\text{g/L}$) in the LARV

	Record Start Date	Record End Date	N	Maximum	Minimum	Average	Median	Skewness
Dissolved Se in Arkansas River	10/5/1988	2/18/1998	166	48	0	11.9	11.0	1.47
Dissolved Se in Tributaries	10/5/1988	5/29/2008	984	1240	0	39.9	12.0	5.18
Total Se in Arkansas River	1/9/1968	6/30/1988	555	90	0	12.3	10.0	2.12
Total Se in Tributaries	1/9/1968	7/23/2004	705	1100	0	23.8	12.3	9.92

3.2.2 USGS Irrigation Return Flow Study on the LARV 1976-1978

A study by the USGS of irrigation return flows and their effect on water quality during the 1976, 1977, and 1978 irrigation seasons was reported by Cain (1985). The study area encompassed the entire LARV from the Pueblo Reservoir to the Colorado-Kansas state line, including 54 irrigation return sites, 41 Arkansas River sites, 5 tributary sites, and a more-extensively studied region located near Holly, CO. While there were not any Se samples taken, this study did gather other surface water data including pH, specific conductance, dissolved oxygen, dissolved sulfate, and dissolved nitrogen (as nitrite plus nitrate). Table 3.3 displays basic statistics of selected constituents taken from the Arkansas River as part of this study.

Table 3.3. Data Summary of Arkansas River Samples for Cain (1985)

	N	Maximum	Minimum	Average	Median	Skewness
Specific Conductance (dS/m)	88	5.900	0.200	2.370	1.885	0.422
Dissolved Oxygen (mg/L)	51	13.2	4.0	8.57	8.1	0.248
Dissolved Sulfate (mg/L)	5	2700	520	1664	2000	-0.336
Dissolved Nitrogen (NO_2+NO_3) (mg/L)	11	4.0	0.01	1.67	1.5	0.485
Total Dissolved Solids (mg/L)	5	4260	957	2713	3240	-0.387

Specific conductance was reported to be inversely related to streamflow with the highest values being recorded in the low flow periods of spring and later summer. It was also reported that during the irrigation season large downstream increases in specific conductance were seen. The dissolved oxygen (DO) concentrations ranged from 4.0 to 13.2 mg/L in the Arkansas River and 3.4 to 16.8 mg/L in irrigation return flows. It was concluded that the Arkansas River was entirely comprised of return flows downstream of the town of Manzanola, CO and that specific conductance generally increased downstream paralleling the amount of return flows.

Furthermore, results indicate that 50% of the salt load to the river came from ground water return flows and the other 50% from excess surface water return flows from fields.

3.2.3 USGS Water Quality Monitoring 1988

The USGS (Mueller 1991) gathered water samples between June and October of 1988 in the LARV between the Pueblo Reservoir in Colorado and Garden City, Kansas. Water, bottom sediment, and biota of the region were analyzed for 5 ground water sites, 5 reservoir sites, 7 Arkansas River sites, and 2 tributary sites. The 5 ground water samples gathered from the alluvial aquifer between La Junta, CO and Deerfield, KS revealed an average C_{Se} value of 13.4 $\mu\text{g/L}$ and ranged from 4 to 29 $\mu\text{g/L}$. The average C_{Se} value of 8 $\mu\text{g/L}$ over samples gathered in the Arkansas River sampled at seven USGS gauging stations between Pueblo, CO and Deerfield, KS was much smaller than the average C_{Se} value of 48.5 $\mu\text{g/L}$ found in tributaries sampled at two USGS gauging stations near Pueblo and Vineland, CO. This indicates that irrigation return flows play a large role in Se loading to the Arkansas River. The average C_{Se} over all surface water samples was approximately 10.0 $\mu\text{g/L}$, with the minimum value of 1 $\mu\text{g/L}$ collected in Pueblo Reservoir and the maximum value of 52 $\mu\text{g/L}$ collected in the St. Charles River near Vineland, Colorado. Table 3.4 shows average constituent concentrations from the ground water, Arkansas River, and tributaries taken during this study.

Table 3.4. Average Constituent Concentrations from Mueller et al. (1991)

	Ground water	Arkansas River	Tributaries
Specific Conductance ($\mu\text{S}/\text{cm}$)	1779	1589	1945
Dissolved Selenium ($\mu\text{g/L}$)	13.4	8.00	48.5
Dissolved Uranium ($\mu\text{g/L}$)	23.1	21.1	17.2
Dissolved Sulfate (mg/L)	760	909	830
Dissolved Nitrogen NO_2+NO_3 (mg/L)	3.98	0.94	3.20
Total Dissolved Solids (mg/L)	1474	1584	1525

While ranging between 2 and 43 µg/g, three of four avian livers gathered from the John Martin Reservoir were higher than 20 µg/g, which is two times greater than the background criterion recommended by Lemly (2002b). Using this limited data set, it was concluded by Mueller et al. (1991) that C_{Se} was increasing downstream along the river and that it was possible that processes occurring in the John Martin Reservoir may be removing dissolved Se from the water and storing it in bottom sediment and/or biota.

3.2.4 USGS Water Quality Monitoring 1990-1993

The USGS (Ortiz et al. 1998) also performed a study of the entire Arkansas River Basin in Colorado, researching a study area of about 6.6 Mha (25,400 square miles) between April 1990 and March 1993. This study area included about 650 km (400 mi) of the main stem of the Arkansas River, with 19 Arkansas River sampling sites, 16 tributary sites, and 2 mine sites. Water sampling occurred approximately 3 times per year, during different flow regimes; low flow (October-April), snowmelt runoff (May-June), and post-snowmelt runoff (July-September). Surface water sampling in the Upper Arkansas River Basin (upstream of Pueblo Reservoir) showed that over 90% of Se samples had concentrations less than 1 µg/L and did not show any potential water quality threat. There were, however, significantly larger total-recoverable Se concentrations in the LARV. Between Pueblo and Las Animas there were 109 surface water samples collected and analyzed for Se, 42 of these having concentrations above the study's chronic total-recoverable Se standard of 10 µg/L. Results from LARV river samples analyzed for total-recoverable Se may be seen in Table 3.5. The two Arkansas River locations with the highest exceedance rates were the Catlin Dam site (58%) and the Las Animas site (71%). The highest median concentration of dissolved Se of 13.5 µg/L was found at the Las Animas site during low flow. Concentrations once again tended to increase in a downstream direction.

However, C_{Se} values decreased just downstream of the John Martin Reservoir. They reported that spatial and temporal Se concentration were a function of local geology, extensive agricultural irrigation, and chemical processes. Also, over 90% of total-recoverable Se was found to be in the dissolved phase.

Table 3.5. Total-recoverable C_{Se} Results in the LARV from Ortiz (1998)

Arkansas River Site Name	N of Samples Taken	N of Samples Above 10 µg/L
Below Pueblo Reservoir	3	0
Pueblo	16	1
Highway 227	3	2
Avondale	16	7
Catlin Dam	24	14
Las Animas	24	17
Below John Martin Reservoir	23	1

3.2.5 KWO Water Quality Monitoring 1995-2000

Whittemore (2000) studied water quality from 1995 to 2000 in the Arkansas River in Kansas for the Kansas Geological Survey. This research addressed salinity as well as other water quality parameters of the Arkansas River corridor in Hamilton, Kearny, Finney, Gray, and Ford counties. The goals of this study were to 1) characterize the water quality of the Arkansas River water entering and flowing in the river corridor in southwest Kansas, 2) determine factors controlling variations in the quality of Arkansas River waters in the corridor, and 3) determine the salinity sources in the Arkansas River, including natural versus human components. All samples were analyzed for specific conductance and dissolved sulfate and chloride concentrations. A subset of samples were analyzed for laboratory pH, alkalinity, and dissolved calcium, magnesium, sodium, potassium, silica, fluoride, nitrate, and boron. This study reported that Colorado's increase in

water consumption caused increased salinity, primarily associated with increased irrigation usage and decreased Arkansas River discharge rates.

3.3 Colorado State University Research on the Water Quality of the Lower Arkansas River

Basin

Colorado State University has been studying irrigation-induced water quality and waterlogging problems in the LARV since 1999. CSU began by first establishing an Upstream Study Region (Figure 3.5) by designating approximately 163 surface water monitoring locations and installing 74 ground water monitoring wells in 1999, followed by adding an additional 23 wells in 2000. This region encompasses the area between the towns of Manzanola, CO and Las Animas, CO and includes approximately 91 kilometers (57 miles) along segment COARLA01b of the Arkansas River, six major irrigation canals, and about 11 major irrigation drains. Approximately 26,400 ha (65,300 ac) of the total 50,600 ha (125,000 ac) regional area is irrigated from canals and unconfined aquifer pumping wells. EC, water temperature, and water table depth (for the wells) were recorded for all locations weekly to biweekly during the irrigation season and monthly to bimonthly during the off season over the period 1999-2008. Data are still being gathered to date but less frequently.

Gates et al (2002) analyzed data over 1999 through 2002 which revealed that the Upstream Study Region had high salinity and water table elevations. The average EC in the Arkansas River was approximately 1.0 dS/m ranging from about 0.85 to 1.5 dS/m. The ground water's average EC was about 3.5 dS/m. The average measured water table depth was only about 2.1 m below the ground surface. Soil salinity measurements gathered using electromagnetic inducing probes during the May to mid-June early irrigation season and early to mid-August late irrigation season

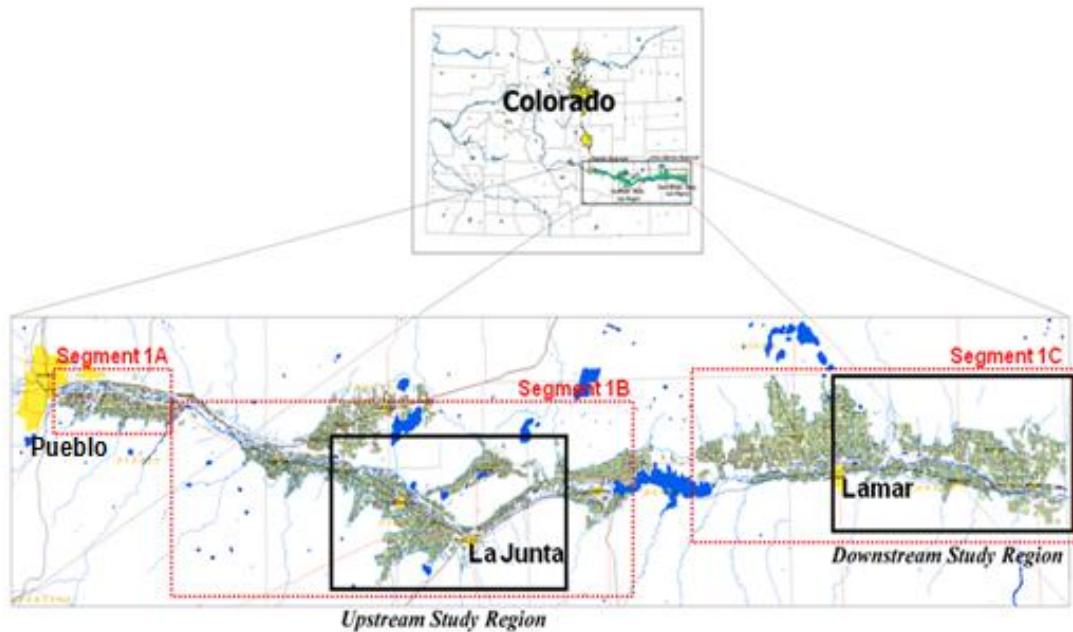


Figure 3.5. General Location of the CSU Upstream and Downstream Study Regions in the LARV

of 1999 indicated that approximately 70 percent of fields exhibited 25 percent or more measurements above the salinity threshold, or the point at which salinity begins to affect crop production. This study also indicated that water table depths greater than 2.5 to 3.0 meters typically were found to have soil salinity below threshold values.

Researchers working on this project initially developed a steady state calibrated ground water and contaminant transport model to estimate implications of water management strategies such as vertical drainage using increased ground water pumping or reducing recharge from excess irrigation application by 20 to 33 percent. While increasing pumping was predicted to only lower the water table by about 0.01 to 0.02 m throughout the region, a 20 and 33 percent decrease in recharge from excess irrigation application was predicted to lower the water table by about 0.36 and 0.62 m, respectively. Simulated ground water salinity, however, was not greatly affected by the 0.36 m water table elevation reduction (Gates et al. 2002).

There were an additional 13 monitoring wells installed in the Upstream Study Region by October 2001. Data collected up to that time were used to develop and calibrate a transient finite-difference ground water flow and contaminant transport model with a weekly time step. The simulated regional average water table depth was 5.75 m in 2000 and 6.10 m in 2001. Salinity decreased as the average water table elevation dropped. This is most likely due to reduced saline ground water up-flux and evapoconcentration. Average ground water salinity was found to be 2805 mg/L in 2000 and 2681 mg/L in 2001. Predicted average soil salinity increased from 2487 mg/L in 1999 to 2805 mg/L in 2000 and reduced slightly to 2681 mg/L in 2001 (Burkhalter and Gates 2005, Gates et al. 2006).

The transient ground water flow and salt transport model was used to evaluate 38 alternatives to lower the ground water table, decrease soil salinity, reduce salt loading to the Arkansas River, increase crop yield, and decrease non-beneficial consumptive use due to upflux from the shallow water table. Solution alternatives considered were irrigation recharge reduction, canal seepage reduction, increased ground water pumping (with increased flows directed to drains), installation of additional sub-surface drainage, or combinations of these solution alternatives. Results from applying the model to the 1999-2001 conditions indicated that the average water table elevation could be reduced by about 2 m by decreasing irrigation recharge by 50 percent, reducing major canal seepage by 90 percent, and installing subsurface relief drains at 50 m spacing and 2 m depth in selected fields. Predicted soil salinity, while likely not reaching equilibrium, decreased over time. The previously used alternative of decreasing irrigation recharge by 50 percent, reducing major canal seepage by 90 percent, and installing subsurface relief drains at 50 m spacing and 2 m depth in selected fields was predicted to decrease average

salinity by 750 to 950 mg/L, increase crop yields by 8 to 10 percentage points, and reduce salt loading to the Arkansas River by 42 percent (Burkhalter and Gates 2006). The model has consistently been updated and refined over the last few years using data gathered from April 1999 through October 2007.

Colorado State University published a technical report (Gates et al. 2006) summarizing the work and results of the first phase of on-going research in the LARV. This report listed three major criteria used as a basis to make decisions; (1) maximize the net economic benefits to agricultural production via reduction in salinity and waterlogging, (2) minimize salt and Se concentrations in the river at key locations, and (3) maximize “liberated” water via reduction in non-beneficial consumptive use from high water tables. The report also listed 14 major findings including estimated canal seepage losses and non-beneficial water use, typical water table depth, existing salinity and Se concentrations, as well as, initial modeling efforts (Gates et al. 2006).

A second study region in the LARV was established in 2002. The Downstream Study Region (Figure 3.5), consisting of approximately 112 monitoring wells and 120 surface monitoring points, has been monitored from 2002 to the present. This region is located along the segment COARLA01c between the town of Lamar, CO and the Colorado – Kansas state line. Approximately 33,000 ha (81,600 ac) of the total 55,200 ha (136,300 ac) in this region is irrigated from canals and unconfined aquifer pumping wells. The Downstream Study Region includes approximately 61.6 kilometers (38.3 miles) of the Arkansas River, six major irrigation canals, and about 11 major tributaries and irrigation drains.

Samples for C_{Se} and related properties and constituent concentrations began being taken from a subset of the ground and surface water monitoring infrastructure in the Downstream Study Region seven times per year in 2003. As seen in Figure 3.6, there are 47 ground water monitoring wells, 12 surface water locations in tributaries and drains, and 6 surface water locations along the Arkansas River that have been routinely monitored since April 2003. In addition, there are 59 ground water observation wells that have been monitored aperiodically.

Sampling for C_{Se} and related properties and constituent concentrations began in the Upstream Study Region in June 2006. A subset of the water monitoring infrastructure described in Burkhalter and Gates (2005) and Gates et al (2006) was selected as the routine monitoring location set for the Se study. Figure 3.7 shows the routinely-sampled locations of 45 ground water monitoring wells, 4 surface water locations in tributaries and drains, and 10 surface water locations. There were an additional 61 ground water observation wells that were monitored aperiodically in this region. Sampling events typically occur during every month of summer (May, June, July, and August), once during the fall (November), once during the winter (December or January), and once during the spring (March). Currently, sampling events alternate between the Upstream and Downstream Study Regions, resulting in each region being sampled 3-4 times per year. Tables 3.6 and 3.7 list sampling event summary information for the total period of study through May 2009.

In-situ water quality parameters including temperature, EC, water table depth, pH, dissolved oxygen (DO), and oxidation reduction potential (ORP), as well as the laboratory analyzed constituent dissolved Se concentration (C_{Se}) have been determined routinely. Laboratory analyzed concentrations of dissolved uranium (C_U), dissolved iron (C_{Fe}), dissolved selenite (C_{SeO_3}),

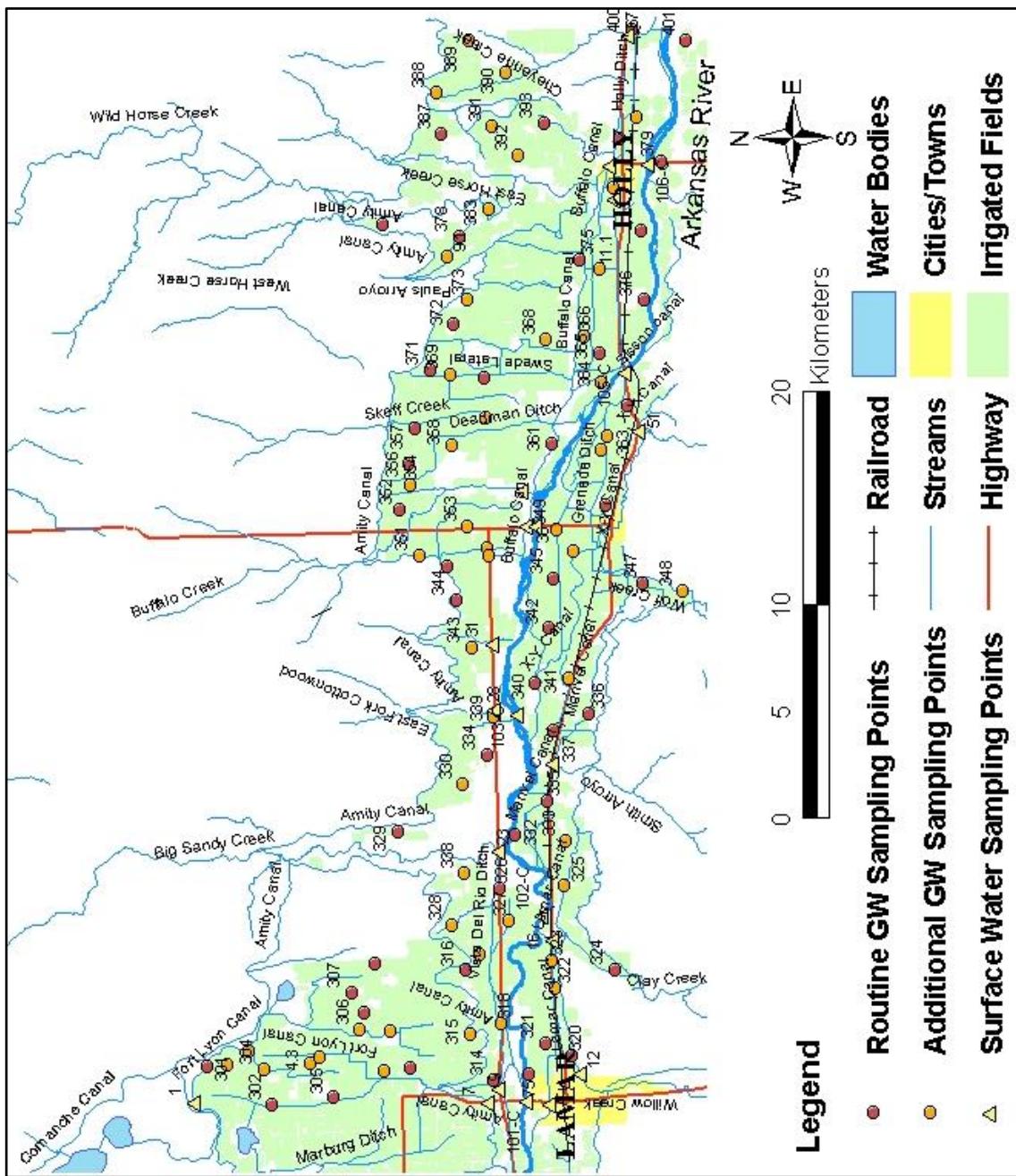


Figure 3.6. Map of the Downstream Study Region showing sampling sites for C_s and related properties and constituent concentrations

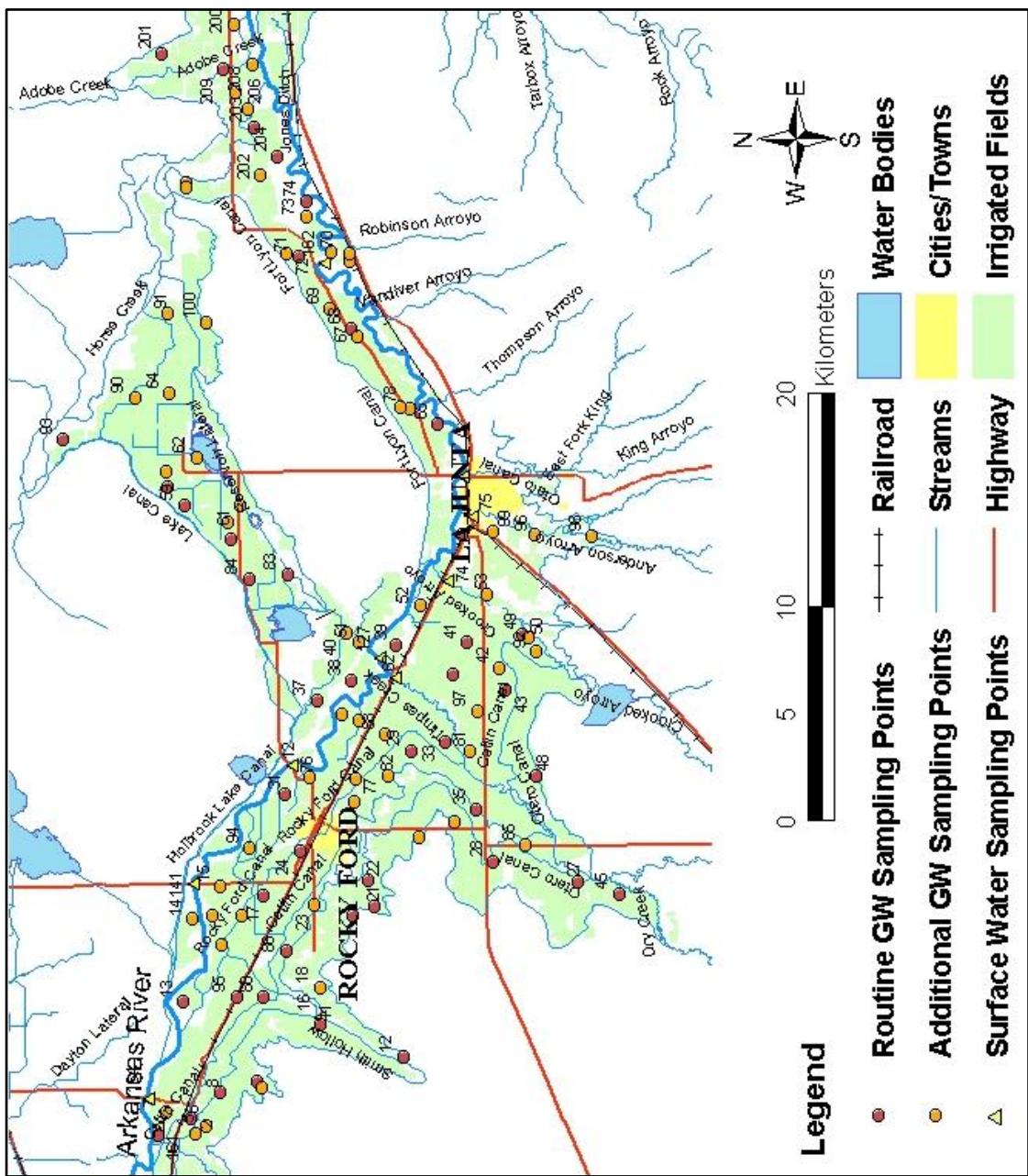


Figure 3.7. Map of the Upstream Study Region showing sampling sites for C_s and related properties and constituent concentrations

Table 3.6. Downstream Study Region Sampling Event Summary

Date of sampling events	Wells Sampled	Dry Wells	Sampled Canals and Drains	Dry Canals and Drains	Arkansas River	Blinks	Duplicates	Total
April 25-May 5, 2003	45	4	7	8	9	7	7	87
May 29-June 11, 2003	44	4	12	3	10	6	6	85
June 30-July 8, 2003	44	5	11	4	7	4	5	80
July 27-31, 2003	42	7	10	5	7	5	5	81
Oct. 25 – Nov. 2, 2003	44	6	9	6	6	5	5	81
Jan. 12-16, 2004	47	6	4	11	6	6	6	86
March 15-18, 2004	47	7	9	6	6	7	6	88
April 30-May 3, 2004	47	7	12	3	6	6	6	87
June 1-4, 2004	46	7	12	3	6	5	5	84
June 28-July 1, 2004	48	6	13	2	6	4	5	84
August 2-5, 2004	51	3	11	4	6	5	5	85
November 4-8, 2004	50	4	12	3	6	6	7	88
January 10-14, 2005	51	3	6	9	6	6	6	87
March 14-20, 2005	48	6	10	5	6	6	6	87
June 27 - July 2, 2005	49	5	13	6	6	5	7	91
July 18-23, 2005	49	5	10	6	6	7	7	90
August 15-22, 2005	47	7	14	2	6	7	7	90
November 19-22 & December 3, 2005	44	8	9	7	6	6	10	90
January 10-14, 2006	42	13	9	7	6	6	11	94
March 10-15, 2006	43	11	7	9	6	7	8	91
May 13-17, 2006	47	12	10	6	6	7	8	96
June 12-16, 2006	45	16	10	6	6	6	8	97
July 10-13, 2006	48	13	11	5	6	3	10	96
August 7-10, 2006	46	15	12	4	6	4	10	97
November 18-20, 2006	47	14	8	7	6	5	9	96
March 9-11, 2007	43	26	9	10	6	4	11	109
May 15-18, 2007	50	19	13	6	6	5	8	107
June 18-22, 2007	58	11	12	5	6	4	7	103
July 22-24, 2007	51	10	15	1	6	3	5	91
August 14-15, 2007	46	15	14	2	6	3	6	91
November 17-19, 2007	47	14	13	3	6	5	7	95
January 15-17, 2008	40	20	11	5	6	4	6	92
May 20-23, 2008	39	11	13	3	6	3	7	82
July 12-16, 2008	34	5	13	3	6	4	7	72
November 20-21, 2008	42	8	12	4	6	3	7	82
March 12-14, 2009	36	10	8	8	6	3	6	77
Total:	1647	343	384	187	225	182	252	3219
Average:	46	10	11	5	6	5	7	89

Table 3.7. Upstream Study Region Sampling Event Summary

Date of sampling events	Wells Sampled	Dry Wells	Sampled Canals and Drains	Dry Canals and Drains	Arkansas River	Blinks	Duplicates	Total
June 17-20, 2006	47	12	4	2	10	7	5	87
May 21-24, 2007	51	11	3	3	10	4	5	87
October 6-11, 2007	37	15	3	1	10	3	5	58
March 17-22, 2008	31	4	4	0	10	3	7	59
June 21-26, 2008	74	3	4	0	8	7	10	106
August 14-15, 2008	43	4	4	0	10	3	6	70
January 15-17, 2009	31	7	3	1	9	3	6	60
May 13-14, 2009	34	7	4	0	10	3	6	64
<i>Total:</i>	348	63	29	7	77	33	50	591
<i>Average:</i>	44	8	4	1	10	4	6	74

total recoverable (dissolved plus adsorbed on suspended sediment) Se ($C_{Se-trec}$), total recoverable iron ($C_{Fe-trec}$), sodium, C_{Na} ; calcium, C_{Ca} ; magnesium, C_{Mg} ; potassium, C_K ; nitrate, (C_{NO_3}); sulfate, (C_{SO_4}); chloride, C_{Cl} ; carbonate, (C_{CO_3}), bicarbonate, (C_{HCO_3}), boron, C_B , and total dissolved solids (TDS) have been aperiodically monitored. Tables 5.1, 5.2, and 5.3, located in Chapter 5, provide the number of samples taken for each constituent as well as the basic statistics.

Donnelly (2005) presented early results from the CSU Se study over the period between April 2003 and November 2004. His thesis included Se background knowledge, project set-up information, and sampling methodologies, as well as results and analysis from data gathered in the first twelve sampling events at the Downstream Study Region.

Donnelly (2005) found that C_{Fe} levels in the Downstream Study Region were low and therefore not a threat to the ecosystem. As a result, sampling for C_{Fe} was discontinued. C_{Se} , however, was found on average to be above established standards and widely varied spatially throughout the

Downstream Study Region. Correlations between C_{Se} and various other constituent concentrations also were explored using the dataset. For example, C_{Se} was found to be moderately correlated ($r_p > 0.3$) with EC, C_{Mg} , C_B , and C_{SO_4} in ground water and with EC, TDS, C_B , C_{SO_4} , and C_{NO_3} in surface water. Also, over 90 percent of C_{Se} was found to be in the form of selenate. Attempts to find predictive relationships between C_{Se} , C_{NO_3} , and C_{SO_4} were made with varying degrees of success. Also, a preliminary mass balance of Se in the Downstream Study Region was completed for the period between April 1, 2003 and March 31, 2004. It was estimated that the Se mass inflow into the study region from the Arkansas River was approximately 145 kg per year while the outflow was about 663 kg per year. Se mass loading from irrigation canals to the Arkansas River was estimated to load more Se into the Arkansas River than subsurface seepage, surface runoff, and tributary flow, combined.

Collection and analysis of data has continued without hiatus through the present time. Gates et al. (2009) reported findings from the start of Colorado State University's Se project in 2003 until August 2008, giving constituent statistics and relationships for this period. This thesis encompassed the period between April 2003 and May 2009 and discusses all findings reported in Gates et al. (2009) in extended detail.

Mueller-Price and Gates (2008) developed stochastic mass-balance models using CSU's acquired dataset in an effort to determine non-point source (NPS) loading of TDS and Se to reaches of the Arkansas River. The average mean Se loading rate to the Arkansas River in the Downstream Study Region was estimated to be 0.038 (kg/day)/km. It was reported that measurement error, spatial variability, temporal variability, and ambiguity in relationships between parameters were major sources of model parameter uncertainty. Several suggestions were made in regards to

reducing uncertainty. These included 1) consider possible internal sinks and sources, 2) enhance and increase frequency of sampling, 3) improve statistical characterization of random parameters, and 4) refine the mass transport model in regard to flow, transport, and chemical processes.

In an effort to analyze the feasibility and impacts of water management alternatives, Triana (2010a, 2010b) developed a GIS-based river basin decision support system (DSS) and applied it to the LARV. The primary objective of the DSS is to assess basin-scale strategies for improving agricultural productivity, salvaging water from non-beneficial consumptive use, and reducing solute concentrations while maintaining compliance with decreed water rights and the Arkansas River Compact between Colorado and Kansas. This DSS provides “1) data import from different sources, 2) automated water rights processing and implementation, 3) alternative points of diversion and storage contracts modeling, 4) an innovative stream-aquifer modeling methodology employing artificial neural networks, 5) automated hydrologic calibration and user-controlled water quality calibration, and 6) management simulation based on the calibration results” (Triana 2010a). A companion paper (Triana 2010b), discussing results given by the DSS in evaluating proposed water resources strategies, states that “conditions favorable to increased agricultural productivity and water conservation can be accommodated, along with the benefits of improved river water quality through reduction of excess irrigation recharge and canal seepage and augmented subsurface drainage, without violating existing water rights and the Colorado-Kansas Interstate Compact Agreement”. Continued research in this area aims to apply a ranking process to these alternatives with respect to the cost and benefits to rural communities.

Chapter IV

METHODOLOGY OF DATA COLLECTION

Though the project supporting this thesis has been ongoing since April 2003, the information in this chapter describes the materials and methods used between August 2007 and May 2009.

While the vast majority of this project's materials and methods have been preserved, there have been a few minor changes regarding the equipment decontamination procedure over the life of the project. Reasons for these changes will be explained as they are presented.

4.1 Sampling Sites

Starting from June 17, 2006 and June 27, 2005 the project has consistently monitored 14 and 22 surface water locations in the Upstream and Downstream Study Regions, respectively. The Upstream Study Region contains 4 tributary/drain and 10 Arkansas River locations while the Downstream Study Region has 12 tributary/drain, 4 canal, and 6 Arkansas River locations. Surface water monitoring locations and descriptions for the Upstream and Downstream Study Regions are presented in Tables 4.1 and 4.2, respectively.

Since June 17, 2006 and January 10, 2006 there have been 52 and 61 ground water locations in the standard well sampling set in the Upstream and Downstream Study Regions, respectively. The observation wells are cased with 0.064 m (2.5 in) inside diameter perforated (slotted) PVC. Each casing is capped on the bottom and slotted along the entire length of the well extending

Table 4.1. Upstream Study Region Surface Water Monitoring Locations

<i>ID</i>	<i>Northing (m)</i>	<i>Easting (m)</i>	<i>Description</i>
12	4213623	615435	Arkansas River, sampled just upstream of the Hwy 266 bridge about 1.5 km north of Hwy 50
16	4212323	603623	Patterson Hollow, sampled just upstream of the County Rd. FF bridge about 0.2 km east of County Rd. 14
62	4208840	619493	Timpas Creek, sampled just upstream of the Hwy 50 bridge about 1 km west of Swink, CO
74	4206404	624073	Crooked Arroyo, sampled just upstream of the Hwy 50 bridge about 2 km west of La Junta, CO
75	4205238	627100	King Arroyo, sampled just upstream of the Hwy 50 bridge in La Junta, CO
95	4205627	628989	Arkansas River, sampled just upstream of the Hwy 109 bridge just north of La Junta, CO
127	4209536	620443	Arkansas River, sampled just upstream of the County Rd. 24.5 bridge about 1 km north of Swink, CO
141	4218285	609844	Arkansas River, sampled just upstream of the Hwy 71 bridge about 1 km north of County Rd. JJ
161	4219919	598455	Arkansas River, sampled off south river bank just north of County Rd. 11 dead-end about 1.5 km north of Hwy 50
162	4212115	638953	Arkansas River, sampled off north river bank just south of Hwy 194 about 1.0 km east of County Rd. 35
163	4220105	592579	Arkansas River, sampled just upstream of the County Rd. 7.25 bridge about 0.5 km north of Hwy 50
164	4220340	599799	Arkansas River, sampled just upstream of the Hwy 207 bridge about 2 km north of Hwy 50
167	4218977	602572	Arkansas River, sampled off south river bank just north of County Rd. 13.5 dead-end just before Rocky Ford Canal diversion
201	4216419	656088	Arkansas River, sampled just upstream of the Hwy 50 bridge in Las Animas, CO

from ground surface to the bottom. The slot area is about 65.6 cm² per linear meter along the well casing. Bentonite clay has been placed around the annulus of the well at the ground surface to discourage entry of surface water. Typically, the total depth of the observation wells falls between 2 to 20 m below the ground surface. Initially well locations were selected using stratified random sampling. This involved discretizing the study region according to field boundaries and using a random number generator to select a subset of fields to be equipped with monitoring wells. After receiving permission from landowners, minor adjustments to the

Table 4.2. Downstream Study Region Surface Water Monitoring Locations

<i>ID</i>	<i>Northing (m)</i>	<i>Easting (m)</i>	<i>Description</i>
1	4235734	708789	Fort Lyon Canal, sampled just upstream of the Hwy 196A bridge north of Lamar, CO
7	4221999	708799	Amity Canal, sampled just upstream of the Hwy 196A bridge north of Lamar, CO
9	4221524	709444	May Valley Drain, sampled just upstream of the Hwy 196A culvert north of Lamar, CO
12	4217685	710111	Willow Creek, sampled just upstream of the County Rd. 9 bridge east of Lamar, CO
16	4218962	716381	Clay Creek, sampled just upstream of the Hwy 50 bridge just east of County Rd. 12
23	4221484	720549	Big Sandy Creek, sampled just upstream of the large culvert under Hwy 196 near County Rd. 15
24	4218991	724704	Smith Arroyo, sampled just upstream of the Hwy 50 bridge located about 3 km west of County Rd. 19
28	4221682	727232	Cottonwood Creek, sampled just upstream of the Hwy 196A bridge just east of County Rd. 19
31	4221790	730336	Boggs Creek, sampled just upstream of the Hwy 196A bridge about 3 km west of County Rd. 22
36	4220178	735826	Buffalo Canal, sampled just upstream of the Hwy 385 bridge just north of the Arkansas River
37	4220404	737494	Buffalo Creek, sampled just upstream of the County Rd. JJ bridge about 1 km west of County Rd. 26
51	4214959	740349	Granada Creek, sampled just upstream of the Hwy 50 bridge about 2 km west of County Rd. 28
57	4216079	751205	Wild Horse Creek, sampled just upstream of the middle of three culverts off County Rd. 34 in Holly, CO
67	4215423	758940	Cheyenne Creek, sampled just upstream of the Hwy 50 bridge about 0.5 km west of the Kansas-Colorado state line
68	4216339	752805	Buffalo Canal, sampled just upstream of the County Rd. 35 bridge about 0.5 km west of Hwy 50
75	4219149	708714	Lamar Canal, sampled just upstream of the Hwy 287 bridge just north of Lamar, CO
101	4220223	708822	Arkansas River, sampled just upstream of the Hwy 287 bridge in Lamar, CO
102	4219449	717524	Arkansas River, sampled just upstream of the County Rd. 13 bridge about 0.5 km north of Hwy 50
103	4220619	726972	Arkansas River, sampled just upstream of the County Rd. 19 bridge about 2 km north of Hwy 50
104	4219765	735837	Arkansas River, sampled just upstream of the Hwy 385A bridge about 3.5 km north of Granada, CO
105	4215610	743052	Arkansas River, sampled just upstream of the Hwy 50 bridge about 0.5 km west of County Rd. 29.5
106	4214513	752873	Arkansas River, sampled just upstream of the Hwy 196A bridge about 1 km south of Holly, CO

initial well locations were made to insure year-round sampling accessibility. Approximate coordinates for ground water monitoring well locations for both the Upstream and Downstream Regions are presented in Tables 4.3 and 4.4, respectively.

Table 4.3. Upstream Study Region Monitoring Well Locations

<i>ID</i>	<i>Depth</i> (m)	<i>Northing</i> (m)	<i>Easting</i> (m)	<i>ID</i>	<i>Depth</i> (m)	<i>Northing</i> (m)	<i>Easting</i> (m)
1	2.65	4219947	597987	49	4.24	4202877	621473
6	5.09	4218390	598743	55	5.15	4205690	626175
8	8.96	4217023	599990	59	7.65	4218720	627524
9A	2.83	4215331	600470	60A	6.22	4216508	625933
11	5.06	4212328	603166	65	2.47	4206846	631340
12	9.33	4208492	601672	67	2.86	4210605	635431
13	3.47	4218760	604215	68	9.39	4210883	635777
17	3.05	4215030	609200	71	10.48	4213384	639210
20	3.2	4210809	608286	72	12.68	4213914	639344
21	2.93	4209805	608734	74	3.2	4212981	641789
22	4.91	4210092	609898	75C	2.67	4211008	639355
24	5.61	4213300	611289	79X	3.32	4206125	619556
27	5.27	4200291	609890	80	5.79	4214991	604467
28	6.13	4204269	610824	83	2.77	4213890	624269
29	3.08	4208101	615959	84	6.71	4215679	624087
31	2.9	4214009	613996	86	4.91	4213938	606614
33	8.08	4206494	616429	87A	7.92	4219502	628347
35	2.99	4205067	613225	92	3.26	4202261	620684
37	6.92	4212506	618367	93	4.79	4224379	630623
38	7.22	4210904	619305	95	4.72	4216245	604444
39	5.88	4208802	620961	201	2.56	4219767	648718
41	2.35	4205505	621068	203	4.02	4215456	645257
42	1.62	4203982	619891	204	4.21	4214334	643881
43	2.99	4203694	618853	207B	2.99	4218628	642457
45	10	4198386	609257	208	2.8	4215537	648183
48	8.2	4202288	614867	209	4.08	4216873	647962

4.2 Equipment and Sampling Methods for Surface and Ground Water

In-situ measurements of pH, temperature, DO, EC, and ORP were taken from surface water locations (Figure 4.1) by typically inserting an *YSI 600QS Multiparameter Sampling System*TM into the center of the stream at about halfway between the water surface and the stream bottom. If it was not possible to reach the center of the stream the YSI was inserted as far from the bank as possible into flowing water. Once this was completed, water samples were taken using a

peristaltic pump (Figure 4.2). A weight was attached to a 25 ft long ¼ inch diameter polyethylene tube. This was lowered into the water and a sample was drawn out using the pump. All dissolved constituent samples were filtered through disposable in-line 30 cm² or 609 cm² 0.45-µm capsule filters (QED Environmental Systems, Part # FF8100 for the 30 cm² or # FF8200 for the 609 cm²). A detachable fitting was attached to the outflow tube enabling the attachment of the filter. Samples taken for total recoverable constituents were unfiltered.

Table 4.4. Downstream Study Region Monitoring Well Locations

<i>ID</i>	<i>Depth</i> (m)	<i>Northing</i> (m)	<i>Easting</i> (m)	<i>ID</i>	<i>Depth</i> (m)	<i>Northing</i> (m)	<i>Easting</i> (m)
301	6.55	4235118	710412	345	2.96	4218874	733342
301A	4.21	4233203	711130	347	7.41	4214741	733098
302	5.73	4232081	708600	350A	5.27	4223871	733932
303A	8.66	4232481	710290	350C	4.45	4221949	734406
304A	6.86	4229880	710819	352	10.09	4226086	736556
305	4.85	4229181	708946	356	7.71	4225667	738769
306	2.68	4227984	712185	357	7.74	4225408	740418
306A	5.88	4227780	712939	359J	5.73	4222155	742804
306AA	3.2	4226592	712043	361	13.26	4218979	739696
307	8.08	4228346	713874	362	2.38	4216652	739403
307A	7.19	4226568	712071	362A	8.23	4216441	736782
308A	3.57	4227271	715231	363A	7.16	4215429	741458
312AA	10.7	4225636	710318	365	2.9	4216755	743906
314	3.32	4221695	709789	371	7.5	4224701	743129
316	3.26	4223042	714928	372	6.86	4223571	745274
319A	6.03	4220080	710072	375	7.1	4217690	748340
320	3.44	4218078	710935	375G	2.32	4217153	748281
321	3.66	4219290	711516	376	2.9	4214684	746418
324	5.21	4216058	714940	376A	2.83	4214789	749680
325	9.6	4218418	718911	378	8.93	4223304	749394
326	2.07	4221397	718775	379	2.86	4213853	752919
329	9.33	4226213	721425	383	3.9	4221939	750717
332	5.88	4220675	721307	385	8.23	4226901	750015
334	3.23	4222038	725020	387	5.79	4224157	754230
335	4.75	4219161	722906	388	4.36	4224397	756207
336	7.89	4217279	726990	392	7.28	4220563	753237
337	11.22	4218896	726183	393	4.94	4219365	754712
340	3.2	4219750	728417	397	2.96	4215810	753986
342	3.57	4219101	730995	400	6.1	4215254	759119
344	6.98	4223481	732313	401	3.11	4212686	758650



Figure 4.1. Recording in-situ water quality parameters at a surface water location

Samples were placed in clean 120 mL or 250 mL plastic (polypropylene or polyethylene) bottles, appropriate for storing dissolved metals. All samples were immediately placed in a cooler containing ice or cold packs. Ice and cold packs were replaced as needed throughout sampling and immediately before shipping samples to laboratories for analysis.



Figure 4.2. Gathering filtered water samples at a surface water location

Ground water samples and in-situ measurements were collected from observation wells using low-flow purging and sampling procedures. First the water level in the well was read using an electronic water level meter and recorded. Next the *QED Sample Pro*TM bladder pump was slowly lowered into the well to avoid disturbing sediments. The pump was placed halfway between the bottom of the well and the water table to collect a composite sample of all water entering the well over the saturated thickness. If possible, the pump intake was kept a minimum of 0.20 m above the bottom of the well to avoid disturbing sediment on the bottom of the well.

The monitoring well was pumped at a rate of approximately 200-300 mL/min. An electronic drawdown indicator was set approximately 0.30 m below the beginning static water level. If the drawdown in the well dropped below this threshold the well was not able to recharge at these pumping rates and purging was reduced to the minimum flow rate specific to the pump - approximately 50-90 mL/min.

Indicator properties (in-situ parameters) of the ground water were measured on time intervals of at least 3 minutes using a flow through cell and *YSI 600QS Multiparameter Sampling System*TM. At least one volume of the flow through cell (approximately 450 mL) was evacuated within each interval. The flow through the well was considered stable when the indicator properties had stabilized for 2 consecutive readings. Indicator properties tolerances were: +/- 0.1 for pH, +/- 3% for EC, +/- 10 mV for ORP, and +/- 10% for DO. Ground water sample collection began when the indicator properties had stabilized. If stabilization could not be attained, samples could be gathered after about 3 well volumes had been purged from the monitoring well. This very rarely occurred, as sampling wells either stabilized or reached the

cutoff drawdown level. Samples of record forms for both surface water and ground water are provided in Appendices A and B, respectively.

Samples for dissolved constituents were collected (Figure 4.3) at a flow rate of approximately 100 to 200 mL/min. Dissolved constituent samples were filtered through disposable in-line 30 cm² or 609 cm² 0.45 µm capsule filters. Samples taken to determine total recoverable constituents were not filtered. Each sample was taken in a clean 120 mL or 250 mL plastic (polypropylene or polyethylene) bottle, appropriate for storing dissolved metals. The cap on the container was removed just prior to capturing the sample discharge. Care was taken not to contaminate the samples when discharging the sampled flow into the containers and not to agitate or aerate the sample flow during containment (to prevent possible oxidation of reduced constituents within the sample). The bottle was tipped at a slight angle to allow the sample discharge to run down the side of the bottle rather than cascading and producing aeration.



Figure 4.3. Gathering filtered water samples at a ground water location

Often two persons would work together while sampling. If this was the case during surface water sampling, one person would record in-situ surface water quality parameters using the YSI 600QS Multiparameter Sampling System™ while the other person would gather water samples using the peristaltic pump. If two persons were sampling ground water, an additional bladder pump was usually taken. One person would record in-situ ground water quality parameters while the other would clean the second bladder pump (as described in Section 4.5). The two would then work together to gather water samples.

4.3 Sample Handling and Custody Requirements

One of the persons gathering the field samples had direct custodial responsibility for collecting, labeling, and mailing all water samples to laboratories for analysis. Chain-of-custody procedures followed the EPA Region VIII “Minimum Requirements for Field Sampling Activities” (1996) protocol. A chain-of-custody record was completed for all samples collected in the field. Each time that samples changed possession, both the person relinquishing and the person receiving the samples would sign, date, and time the chain-of-custody form. Chain-of-custody records were kept in a data file for each sampling event. A sample of a Chain-of-custody form is included in Appendix C.

Samples were put on ice in a cooler after being gathered. Care was taken to change ice or cold packs when needed. Samples were sent to laboratories by 1-2 day service for analysis in this condition.



Figure 4.4. Sampling equipment: (clockwise, beginning at lower left) drawdown meter; pump tubing; ground water pump; sample bottles, large and small water filters, and filter attachment; YSI Sonde; YSI cable and control box; peristaltic surface water pump; and ground water power pack for bladder pump operation.

4.4 Equipment Calibration and Frequency

The *YSI 600QS Multiparameter Sampling System*TM used to collect in-situ measurements was calibrated according to the manufacturer's guidelines. Directly before each day of sampling the

membrane on the DO sensor was replaced and the *YSI 600QS Multiparameter Sampling System*TM was calibrated for pH, DO, and EC. Every six months the *YSI 600QS Multiparameter Sampling System*TM was calibrated for ORP.

The 3-point calibration of pH consisted of inserting the sonde into and calibrating using 3 pH calibration solutions (pH 4.00, 7.00, and 10.00). The sonde was rinsed with deionized water between calibrations solutions. To calibrate for dissolved oxygen the current barometric pressure was entered into the YSI and the sonde was inserted into deionized water. The YSI then stabilized for 40 seconds and the calibration key was entered. EC was calibrated by inserting the sonde into specific conductance calibration solution and entering the calibration key. ZoBell calibration solution was used to calibrate for ORP. The sonde was rinsed with deionized water between each calibration. Complete calibration procedures, general maintenance information, as well as, more detailed information can be found at the YSI website (www.y si.com).

For the sampling periods between August 2007 and May 2009 there was an error in the way the YSI 600QS was calibrated for DO. It was assumed instrument was programmed to automatically calculate and use the in-situ barometric pressure for calibration. This was, in fact, not the case and barometric pressure should have been entered into the YSI 600QS manually each time. The default barometric pressure in the YSI 600QS was 650 mm Hg. The average estimated error in the DO readings taken during this time frame was approximately 2 – 8%.



Figure 4.5. YSI calibration supplies: (left to right) pH 4.00 solution, pH 7.00 solution, pH 10.00 solution, and specific conductivity solution

4.5 Decontamination of Sampling Equipment

The following decontamination process was completed between each sampling location in which pumping equipment was used:

- a. Pre-rinse: If the pump and filter attachment were visibly covered with sediment or other significant stains, they were disassembled and rinsed in a 18.9-liter (5 gal) bucket containing 11.4 liters (3 gal) of potable water (treated tap water). All sample water was evacuated from the pump and visible dirt and debris were removed from the pump components during the pre-rinse process.

- b. Wash: The disassembled pump and filter attachment were washed 3 times in an 18.9-liter (5 gal) bucket containing 11.4 liters (3 gal) of phosphate-free detergent solution for approximately 5 minutes. The solution was composed of approximately 5 ml of detergent added to 11.4 liters (3 gal) of tap water.
- c. First Post-Rinse: The disassembled pump and filter attachment were flushed 3 times in an 18.9-liter (5 gal) bucket containing 11.4 liters (3 gal) of distilled/deionized water.
- d. Final Post-Rinse: The disassembled pump and filter attachment were rinsed 3 times in an 18.9-liter (5 gal) bucket containing 11.4 liters (3 gal) of distilled/deionized water.

The washing/rinsing cycle was previously 5 times per bucket, however, laboratory tests using blanks confirmed that a cycle of 3 washes/rinses per bucket was sufficient for decontamination. Also, the wash/rinse solution volumes were much larger (40 liters), however, this size was determined to be unmanageable for field work and was changed to 11.4 liters (3 gal).

4.6 Analytical Methods

Dissolved concentrations of sodium, C_{Na} (USEPA 1983, Method 273.1); calcium, C_{Ca} (USEPA 1983, Method 215.1); magnesium, C_{Mg} (USEPA 1983, Method 242.1); potassium, C_K (USEPA 1983, Method 258.1); nitrate, C_{NO_3} (USEPA 1983, Method 353.2); sulfate, C_{SO_4} (USEPA 1983, Method 375.4); chloride, C_{Cl} (USEPA 1983, Method 325.1); carbonate, C_{CO_3} (APHA 1992, Method 2320-B); bicarbonate, C_{HCO_3} (APHA 1992, Method 2320-B); and boron, C_B (APHA 1992, Method 4500-B-D) were tested by Ward Laboratories, Inc. (PO Box 788; Kearney NE 68848-0788;

<http://www.wardlab.com>). Ward Laboratories, Inc. participates in the check sample program with the North American Proficiency Testing Program.

Total dissolved Se, selenite, Fe, and total recoverable constituents were tested by the Oscar E. Olson Biochemistry Laboratories at South Dakota State University (Box 2170, ASC 133; Brookings SD 57007-1217; <http://anserv.sdstate.edu/>). Olson Biochemistry Labs are certified by the EPA for drinking water and subscribes to the proficiency testing and check sample programs for the USEPA for wastewaters. Official Methods of Analysis of AOAC International, 17th Edition, test number 996.16 Se in Feeds and Premixes, Fluorometric Method was used to determine the concentration of selenite in the filtered sample. Total recoverable Se concentration, $C_{Se-Trec}$, was determined by first adding hydrochloric acid to the sample to reduce all forms of Se within the sample to selenite and then re-performing the fluorometric analysis on an unfiltered sample. The concentration of selenate was estimated to be the difference between the concentrations of total recoverable Se and selenite. The detection limit for this process was 0.4 µg/L.

Dissolved Fe concentration, C_{Fe} , was determined using Inductively Coupled Plasma (ICP) (EPA Method 200.7) on a filtered sample. Dissolved Fe concentration, C_{Fe} , was determined using acid-microwave digestion (EPA Method 3015) followed by Inductively Coupled Plasma (ICP) (EPA Method 200.7) on an unfiltered sample. The detection limit for both of these methods was about 1 µg/L.

Dissolved U concentration, C_U , was tested by Severn Trent Laboratories (13715 Rider Trl N, Earth City, Missouri 63045 <http://labinc.reachlocal.net>) using ICP mass spectrometry (Methods for Chemical Analysis of Water and Wastes 200.8). The detection limit for this method was 4 µg/L.

4.7 Quality Control

Several quality control measures were put in place in regard to the collection of water samples for this project:

- a. All project personnel responsible for collecting, labeling, storing, and shipping water samples were trained in the associated procedures per the approved Sampling and Analysis Plan for this project.
- b. Equipment blanks were taken of distilled/deionized water samples generated in a laboratory prior to using any piece of equipment in the field. All pump equipment used in the field was first tested on such an equipment blank. If any constituent was detected in the equipment blank at the minimum level specified in the referenced method, the source of the contamination/interference was identified and removed prior to sampling. The equipment was demonstrated to be free from detectable levels of any constituent before field use.
- c. Field blanks were taken to insure that sample contamination had not occurred in the field. Field blanks were collected before each day of sample collection by processing distilled/deionized water through each of the sample steps and field equipment (i.e., tubing, pump, filters, etc. for ground water samples). They were shipped with all other samples to the laboratory for analysis after each event and were not identified as field blanks.

d. Field duplicates were collected to assess the precision of the field sampling and analytical processes. At least one field duplicate was taken every day. Field duplicates were generated by collecting two water samples in rapid succession. They were shipped with all other samples to the laboratory for analysis after each event and were not identified as field duplicates.

4.8 Problems and Challenges Encountered in Field Sampling and Laboratory Analysis

It is very beneficial to be detailed-oriented throughout the entire data acquisition process. The quality of data gathered, as well as the efficiency of time and energy spent in the field, is directly dependant upon a detailed organization of equipment and supplies needed for sampling.

An exhaustive packing list, tailored to each individual sampling event, is needed. Many areas where data are collected are remotely located. There are several items that are crucial to a complete sampling event that are difficult or impossible to find in nearby towns. Some of these include water filters; YSI 600QS parts and calibration solutions; and pump bladders, o-rings, and fittings. When packing, it is very important to check equipment for any possible cause of malfunction. Extensive equipment cleaning and checking before departing on a sampling event may save a large amount time in the field.

When the packing list is completed, an inventory of items on hand should be taken well in advance of the sampling departure date. This will give the sampler ample time to order and receive any needed consumables or equipment. Manufacturers may discontinue items without notice; therefore, item sourcing may be required. It is also important to arrange for a vehicle that is properly maintained and dependable.

When preparing to depart, ensure that all items on the packing list are safely loaded into the vehicle. Special care should be taken with corrosive or otherwise dangerous chemicals. A packed vehicle should not be left overnight. Some equipment may be sensitive to cold or hot weather and there is a possibility of theft. In addition, small amounts of water inside tubes, pumps, or other equipment may freeze and expand, causing damage.

There may be situations where the sampler is required to walk a long distance to the sampling location. In these cases, time may be saved by double checking that all needed equipment and consumables are brought to the location the first time. A good way of doing this is to mentally run through the sampling procedure before departing. When departing from a sampling location double check there are not any equipment or consumables are left at the site.

Water samples should be mailed to laboratories as soon as possible upon returning from each sampling event. Care should be taken that sample labels and chain of custody forms are consistent. It is also important that each laboratory knows exactly which analysis they are to perform. Good records should be kept of all expenditures, including payment of laboratory analysis.

Chapter V

ANALYSIS AND RESULTS

5.1 Statistical Analysis of the Data

5.1.1 Basic Statistical Characterization

Histograms displaying the distribution of specific constituents derived from the analysis of samples collected from routine ground and surface water locations over the life of the project were prepared using STATISTICA® (Version 9.0, StatSoft 2009). As presented in following sections of this chapter, C_{Se} is strongly and significantly correlated with both C_U and C_{NO_3} . Histograms for these three constituents are displayed below and show a large range of constituent concentrations. The distributions of the datasets are substantially skewed and non-normal. Figures 5.1 and 5.2 show histograms of C_{Se} for ground water samples from the Upstream and Downstream Study Regions, respectively, while Figures 5.3 though 5.4 show histograms of C_{Se} for river samples. Histograms of C_{Se} in samples from tributaries and drains in the Upstream and Downstream Study Regions are shown in Figures 5.5 and 5.6, respectively, while Figure 5.7 presents a histogram of C_{Se} in samples from canals in the Downstream Study Region. Histograms for $C_{Fe-Trec}$ and C_{SO_4} are located in Appendix D.

Figures 5.8 through 5.13 present similar histograms of C_U while Figures 5.15 though 5.21 show histograms of C_{NO_3} data. The distributions are quite similar to those of C_{Se} . All datasets are

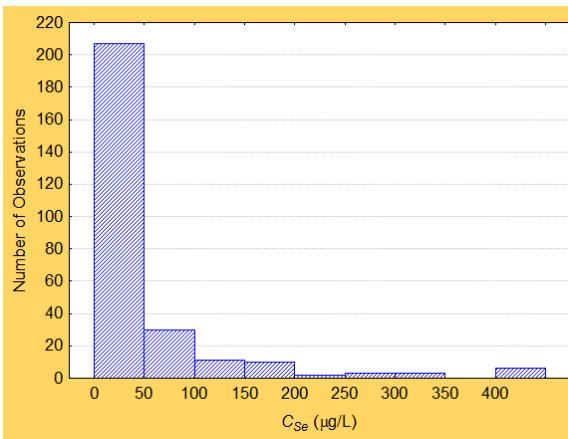


Figure 5.1. Histogram of C_{Se} from routine samples gathered in the ground water of the Upstream Study Region

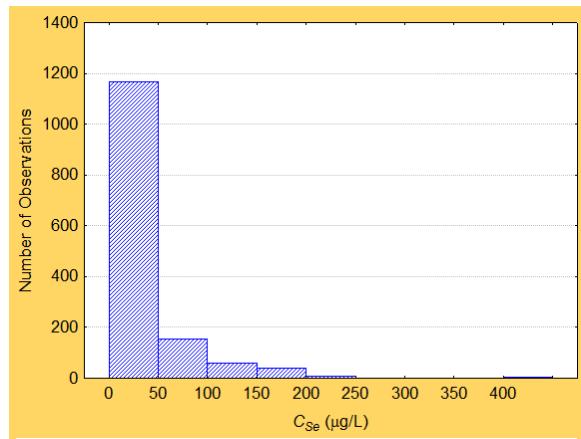


Figure 5.2. Histogram of C_{Se} from routine samples gathered in the ground water of the Downstream Study Region

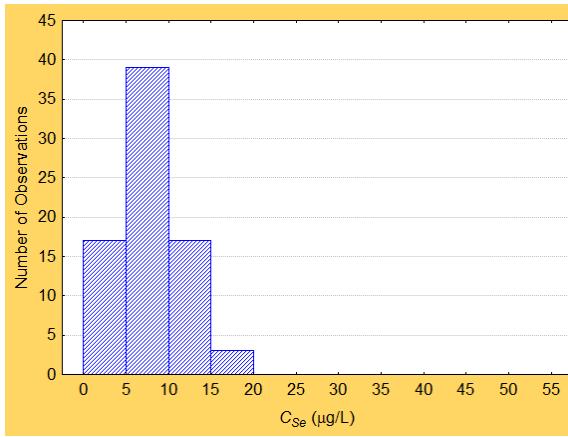


Figure 5.3. Histogram of C_{Se} from routine samples gathered from the Arkansas River in the Upstream Study Region

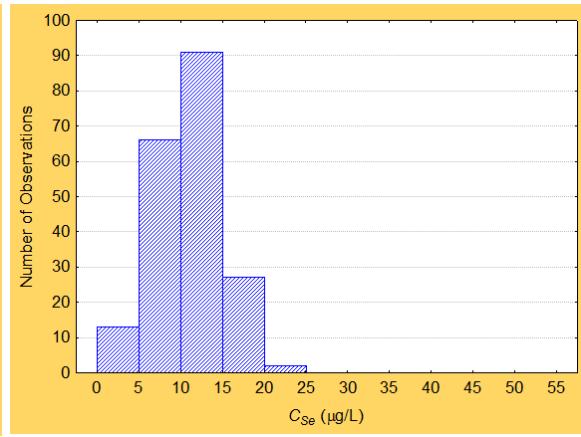


Figure 5.4. Histogram of C_{Se} from routine samples gathered from the Arkansas River in the Downstream Study Region

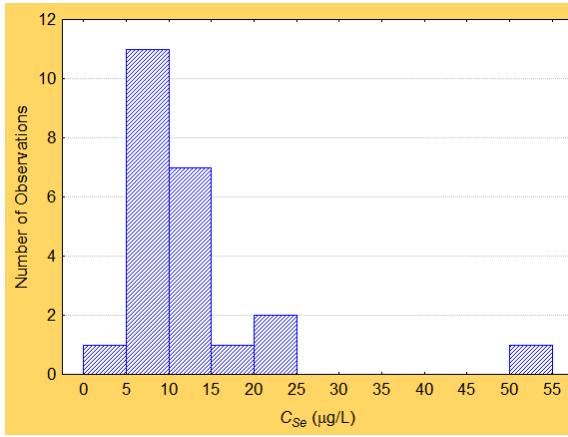


Figure 5.5. Histogram of C_{Se} from routine samples gathered from tributaries and drains in the Upstream Study Region

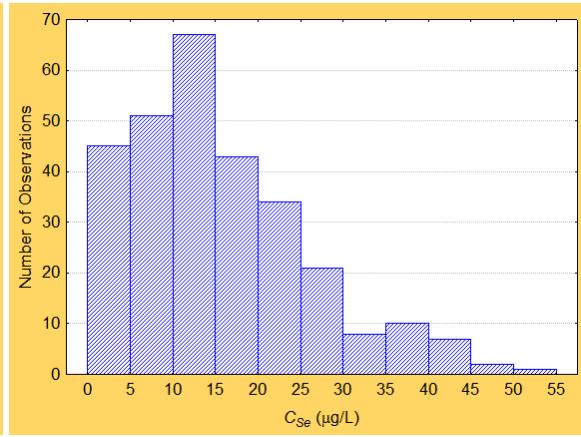


Figure 5.6. Histogram of C_{Se} from routine samples gathered from tributaries and drains in the Downstream Study Region

skewed to the right with large numbers of sample concentrations being at or below the detection limit. Ground water samples are more right skewed than surface water samples in distributions of all three constituents. Ground water samples also tend to have a much larger range of concentration values than surface water.

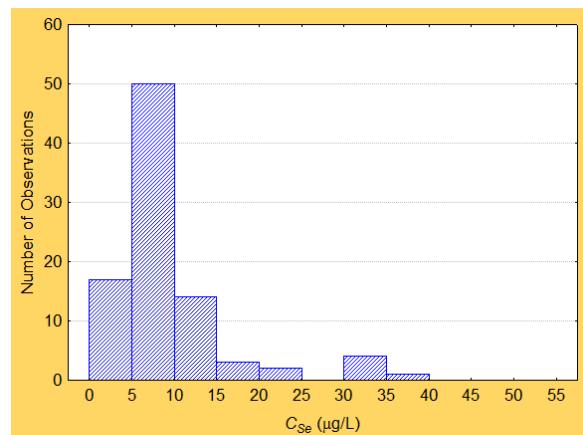


Figure 5.7. Histogram of C_{Se} from routine samples gathered from canals in the Downstream Study Region

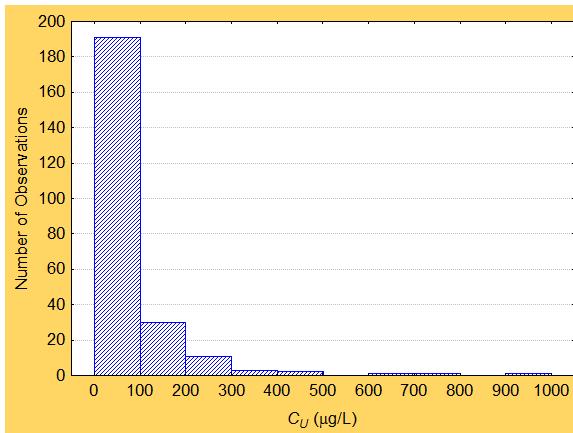


Figure 5.8. Histogram of C_U from routine samples gathered in the ground water of the Upstream Study Region

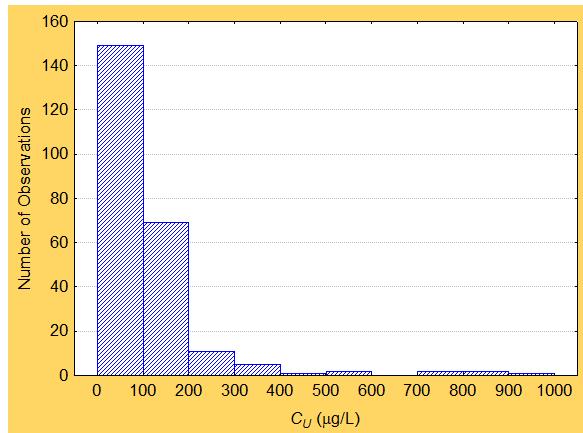


Figure 5.9. Histogram of C_U from routine samples gathered in the ground water of the Downstream Study Region

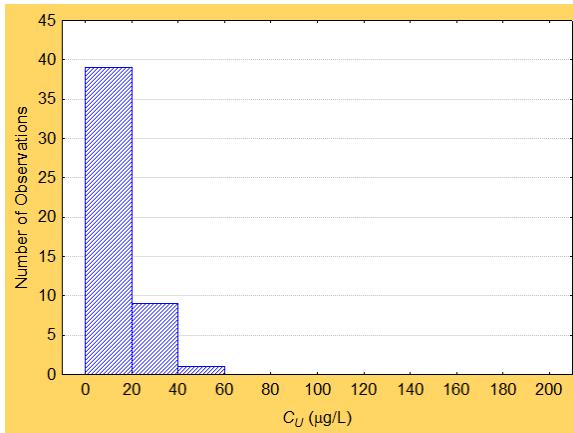


Figure 5.10. Histogram of C_U from routine samples gathered from the Arkansas River in the Upstream Study Region

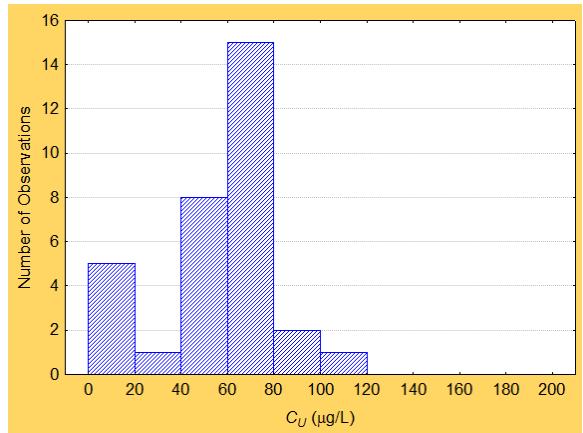


Figure 5.11. Histogram of C_U from routine samples gathered from the Arkansas River in the Downstream Study Region

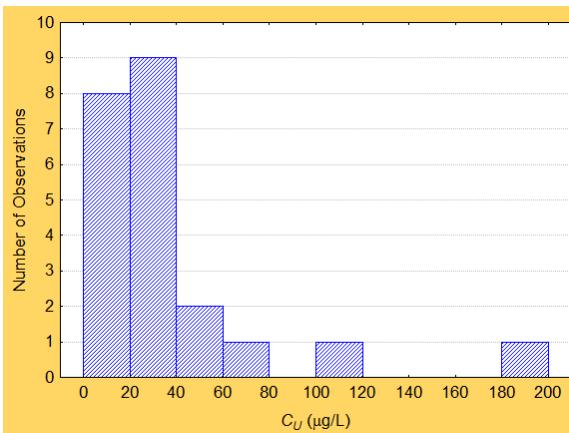


Figure 5.12. Histogram of C_U from routine samples gathered from tributaries and drains in the Upstream Study Region

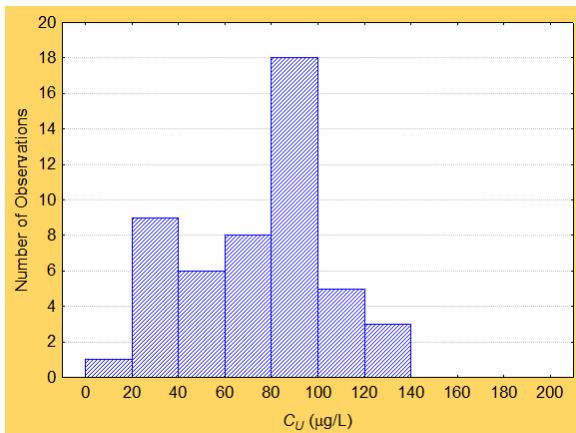


Figure 5.13. Histogram of C_U from routine samples gathered from tributaries and drains in the Downstream Study Region

Chauvenet's criterion (Taylor 1997) was used to test for outliers in the data. This method was rejected, however, after finding that it removed high but seemingly legitimate constituent values. Non-parametric basic statistics, such as the number of samples taken, maximum, minimum, average, median,

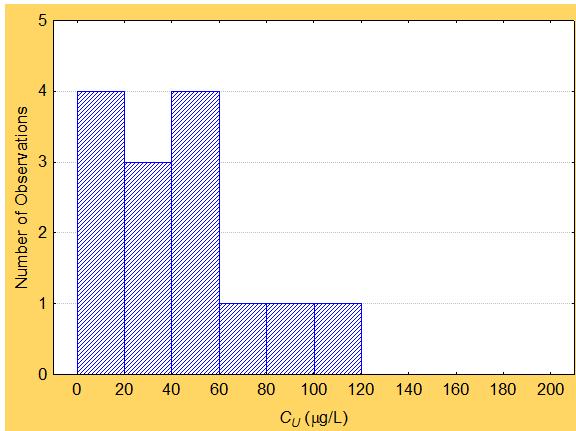


Figure 5.14. Histogram of C_U from routine samples gathered from canals in the Downstream Study

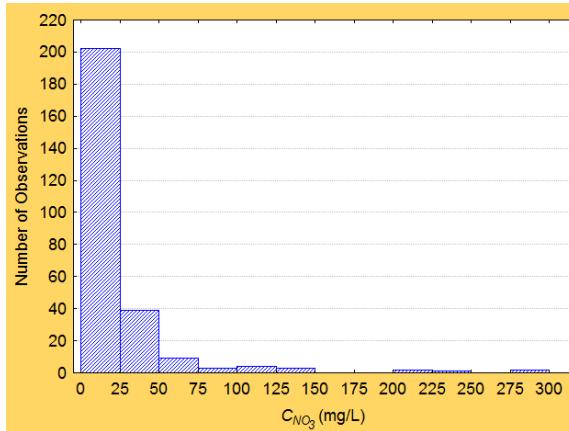


Figure 5.15. Histogram of C_{NO_3} from routine samples gathered in the ground water of the Upstream Study Region

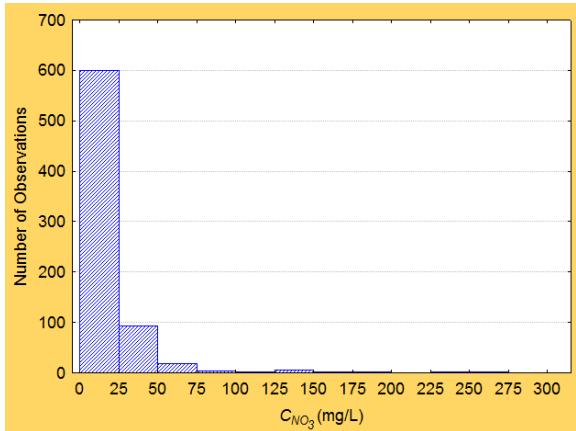


Figure 5.16. Histogram of C_{NO_3} from routine samples gathered in the ground water of the Downstream Study Region

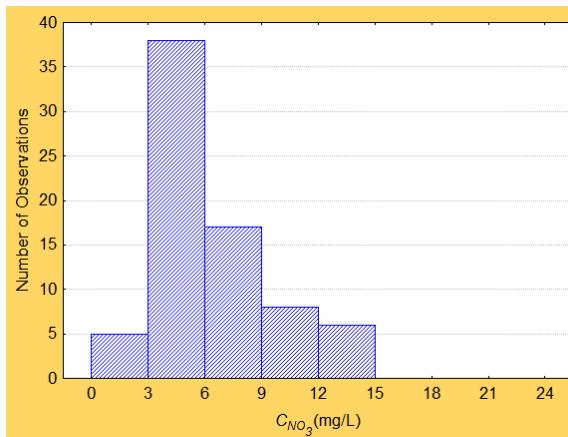


Figure 5.17. Histogram of C_{NO_3} from routine samples gathered from the Arkansas River in the Upstream Study Region

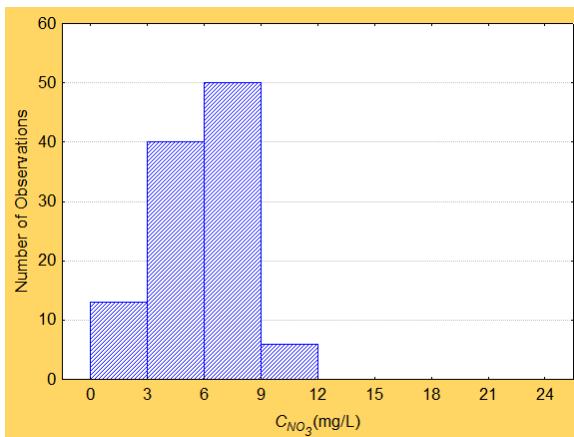


Figure 5.18. Histogram of C_{NO_3} from routine samples gathered from the Arkansas River in the Downstream Study Region

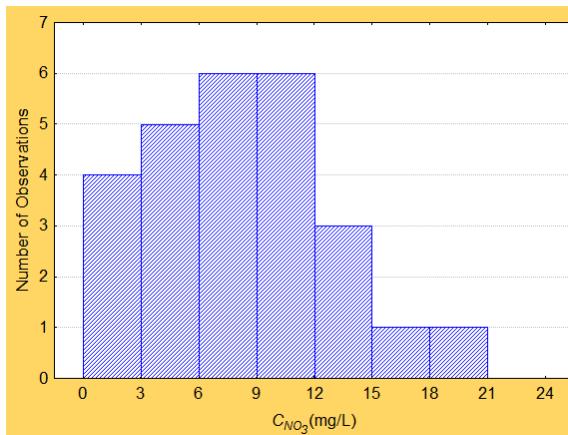


Figure 5.19. Histogram of C_{NO_3} from routine samples gathered from tributaries and drains in the Upstream Study Region

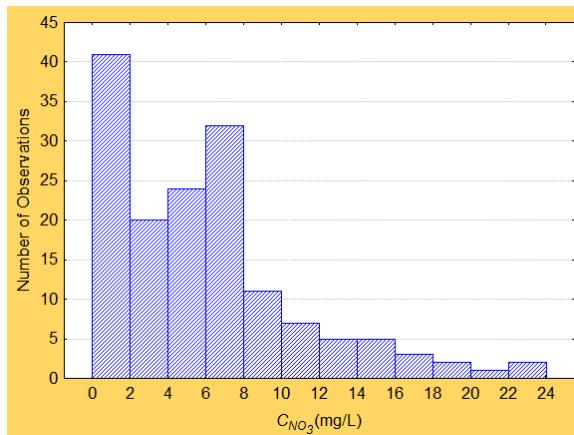


Figure 5.20. Histogram of C_{NO_3} from routine samples gathered from tributaries and drains in the Downstream Study Region

85th percentile, coefficient of variation (CV), and skewness (Gauch 2000), were computed for each sampled constituent. Table 5.1 shows values of basic statistics for ground water samples while Tables 5.2 and 5.3 show values for surface water samples found in the Arkansas River and tributaries/drains, respectively.

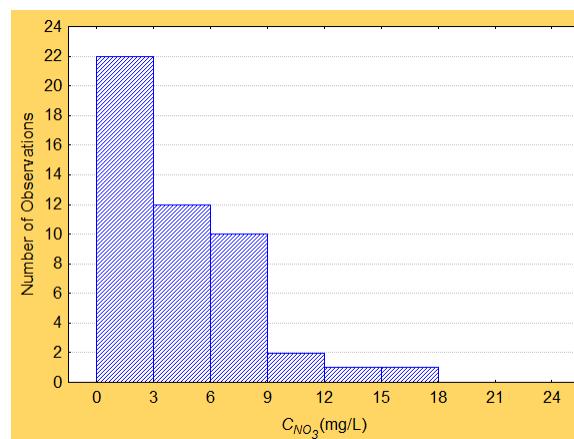


Figure 5.21. Histogram of C_{NO_3} from routine samples gathered from canals in the Downstream Study Region

Values of C_{Se} in both the surface and ground water of the LARV were found to greatly exceed guidelines established by the USEPA and CDPHE. As seen in Table 5.1, the average ground water C_{Se} for routinely monitored wells were 59.9 µg/L and 33.2 µg/L for the Upstream and Downstream Regions, respectively. The maximum C_{Se} values of 1410 µg/L and 3760 µg/L sampled from the Upstream and Downstream Study Regions are approximately two orders of magnitude higher than the CDPHE acute standard of 20 µg/L. The surface water of the LARV also was found to have high C_{Se} values. While the chronic standard for C_{Se} in surface water is currently set by both the USEPA and the CDPHE at 4.6 µg/L (85th percentiles), the 85th percentiles of C_{Se} in surface water samples from the Arkansas River in the Upstream and Downstream Study Regions were 12.6 µg/L and 14.9 µg/L, respectively (Table 5.2). Values of C_{Se} in the tributaries and drains were even higher than those found in the Arkansas River. Average C_{Se} in tributaries and drains were 12.8 µg/L and 15.8 µg/L while average Arkansas River concentrations were 8.0 µg/L and 10.9 µg/L for the Upstream and Downstream Study Regions, respectively (Table 5.3).

Laboratory analysis revealed that selenate was the most dominant form of dissolved Se in samples from the LARV. Analysis was conducted on 116 ground water samples from the Upstream region and 42 ground water samples from the Downstream region for both C_{Se} and selenite concentrations. The concentration of dissolved selenate was estimated to be the difference between the total dissolved Se concentration and dissolved selenite concentration. Selenate accounted on average for approximately 91% and 92%, respectively, of C_{Se} in these ground water samples. The surface water of the Downstream region yielded similar results. On average 81% of C_{Se} was found to be in the form of selenate from the 16 surface water samples tested.

Every average specific ion concentration, with the exception of $C_{Fe-Trec}$ and C_{NO_3} , increased from the Upstream Study Region to the Downstream Study Region in Arkansas River surface water samples. Most of these increases were substantial. TDS increased by 270% and C_U , C_{Na} , C_{Mg} , C_{SO_4} , and C_B each increased by over 300%. This was also the case with average concentration values for tributary and drain surface waters; however, the increases were not as great.

Three other constituents, in addition to C_{Se} , exceeded CDPHE standards. Maximum ground water C_B values of 428 mg/L in the Upstream Study Region and 162 mg/L in the Downstream Study Region greatly exceeded the CDPHE agricultural ground water acute standard of 0.75 mg/L. Maximum surface water C_U values of 197 µg/L in the Upstream Region and 138 µg/L in the Downstream Region greatly exceeded the MCL surface water standard of 30 µg/L. In addition, both regions' 85th percentile $C_{Fe-Trec}$ values greatly exceeded the chronic surface water standard of 1.00 mg/L. The Upstream and Downstream Study Regions were 12 and 2 times this standard, respectively. The CDPHE has not currently set an agricultural ground water standard for C_U or $C_{Fe-Trec}$.

While the CDPHE has not established or assigned any salinity standards for surface water outside the Colorado River Basin, EC in the LARV has been described as high (Mueller-Price 2008). Average Arkansas River EC values of 1081 and 3281 µS/cm were recorded for the Upstream and Downstream Study Regions, respectively. Average ground water values were even higher with 3521 and 4623 µS/cm recorded in the Upstream and Downstream Study Regions, respectively.

Table 5.1. Basic Statistics for Ground water Samples

Constituent/ Property	N	Maximum	Minimum	Average	Median	Percentile	CV	Skewness	N	Maximum	Minimum	Average	Median	Percentile	CV	Skewness	85th
																	Downstream
C _{Si} (µg/L)	272	1410	0.40	59.9	17.6	73.4	265.9%	6.49	1435	474.0	0.40	33.2	17.2	59.0	139.7%	3.66	
C _{Ti} (µg/L)	240	972.0	6.40	80.0	48.0	114.0	134.5%	4.42	242	907.0	11.0	111.8	72.0	164.4	119.5%	3.67	
C _{Va} (mg/L)	271	8188	37.0	439.8	230.0	604.0	196.3%	5.84	767	8514	58.0	647.3	467.0	886.5	102.5%	5.29	
C _{Cr} (mg/L)	271	726.0	65.0	351.9	359.0	507.0	40.2%	-0.08	767	744.0	34.0	384.5	397.0	500.0	28.9%	-0.23	
C _{Ni} (mg/L)	271	4904	19.0	203.6	105.0	287.0	197.8%	7.94	767	2227	29.0	208.1	164.0	292.0	86.1%	4.63	
C _K (mg/L)	271	17.0	0.00	3.32	3.00	5.00	69.7%	2.04	767	256.0	2.00	16.8	13.0	22.0	132.4%	7.80	
C _{Na} (mg/L)	264	292.4	0.44	22.2	10.0	34.1	179.9%	4.24	728	265.4	0.00	16.6	9.7	27.0	154.6%	5.07	
C _{Ca} (mg/L)	271	29450	147.0	1986	1329	2759	145.6%	5.96	767	11330	21.7	2373	2091	32722	63.3%	2.82	
C _{Cr} (mg/L)	271	1024	11.0	96.5	58.0	114.5	145.7%	4.31	767	12890	9.00	213.7	124.0	262.3	273.6%	17.1	
C _{Co} (mg/L)	271	42.0	1.00	1.15	1.00	1.00	216.3%	16.5	767	66.0	1.00	1.33	1.00	1.00	222.7%	15.3	
C _{HCO} (mg/L)	271	1846	158.0	416.2	372.0	523.5	49.8%	3.08	767	1449	148.0	395.4	376.0	509.0	35.1%	2.04	
C _S (mg/L)	271	428.0	0.08	2.07	0.35	0.87	1253%	16.5	767	162.0	0.08	1.06	0.60	1.21	555.7%	26.8	
TDS (mg/L)	271	44600	462.6	3522	2492	4681	125.6%	5.77	767	35550	855.4	4256	3703	5643	66.2%	4.33	
pH	257	7.51	5.29	6.45	6.52	6.89	7.2%	-0.34	1398	8.54	5.28	6.66	6.73	6.98	0.06	-0.45	
T (°C)	257	24.7	6.91	15.0	15.1	18.2	19.8%	0.07	1398	30.4	2.26	15.6	15.6	18.6	19.8%	0.12	
EC (µS/cm)	257	28330	0.85	3521	2830	5040	95.0%	4.71	1396	44370	295.8	4633	4035	6187	64.8%	4.74	
DO (mg/L)	256	9.66	0.00	2.31	1.70	4.38	82.1%	1.35	1379	12.7	0.00	2.82	2.19	5.27	80.3%	1.09	
ORP (mV)	257	334.6	-279.9	85.0	101.6	184.0	124.9%	-0.73	1398	492.4	-334.8	115.4	131.8	195.6	84.7%	-1.43	

Table 5.2. Basic Statistics for Arkansas River Surface Water Samples

Constituent/ Property	N	Maximum	Minimum	Average	Median	Percentile	CV	Skewness	N	Maximum	Minimum	Average	Median	Percentile	CV	Skewness	85th
																	Upstream
$C_{\text{Fe}} (\mu\text{g/L})$	76	16.9	3.28	7.99	7.32	12.6	44.7%	0.72	199	23.0	4.22	10.9	14.9	34.3%	0.12		
$C_{\text{Cr}} (\mu\text{g/L})$	49	49.8	4.70	14.2	10.4	22.4	70.1%	1.74	32	106.0	13.6	57.4	62.1	74.0	39.9%	-0.56	
$C_{\text{Fe-Tot}} (\text{mg/L})$	29	51600	1480	8812	6310	12200	1	3	159	11200	20.0	918	365	2016	139%	3.97	
$C_{\text{Na}} (\text{mg/L})$	76	260.0	19.0	76.3	63.0	114.8	63.0%	1.77	113	636.0	103.0	396.0	394.0	534.0	30.5%	-0.23	
$C_{\text{Ca}} (\text{mg/L})$	76	304.0	44.0	103.2	88.5	141.8	54.9%	1.98	113	419.0	115.0	299.0	309.0	359.2	22.0%	-0.88	
$C_{\text{Mg}} (\text{mg/L})$	76	99.0	14.0	35.3	28.0	54.0	56.4%	1.52	113	213.0	46.0	141.3	141.0	178.8	25.9%	-0.52	
$C_{\text{K}} (\text{mg/L})$	76	5.00	1.00	3.37	3.00	4.00	26.9%	-0.48	113	18.0	4.00	10.0	10.0	12.0	23.2%	-0.11	
$C_{\text{Na+}} (\text{mg/L})$	74	14.6	1.77	6.31	5.32	10.2	49.2%	1.01	109	11.5	0.89	5.82	6.20	7.97	39.5%	-0.16	
$C_{\text{SiO}_4} (\text{mg/L})$	76	1230	18.0	367.1	288.0	563.3	69.0%	1.64	113	2361	486.0	1633	1665	2030	25.0%	-0.78	
$C_{\text{Ca+}} (\text{mg/L})$	76	85.0	8.0	28.1	22.5	42.5	62.4%	1.46	113	169.0	33.0	109.5	114.0	137.2	26.9%	-0.49	
$C_{\text{CaO}} (\text{mg/L})$	76	21.0	0.00	8.47	8.00	13.0	54.3%	0.46	113	184.0	1.00	14.7	13.0	23.0	135.6%	5.69	
$C_{\text{CaCO}_3} (\text{mg/L})$	76	309.0	0.0	161.4	155.0	219.3	38.1%	0.36	113	742.0	134.0	294.4	303.0	346.6	24.7%	1.53	
$C_{\text{S}} (\text{mg/L})$	76	0.29	0.01	0.10	0.09	0.15	58.6%	1.37	113	0.96	0.00	0.49	0.49	0.67	34.2%	-0.14	
TDS (mg/L)	76	2193	231.1	785.1	634.8	1188	56.5%	1.53	113	4103	944.8	2904	2953	3622	24.4%	-0.79	
pH	76	8.79	6.77	8.07	8.09	8.45	0.04	-0.72	200	10.4	6.75	8.04	7.99	8.27	0.06	2.30	
T ($^{\circ}\text{C}$)	76	27.7	2.06	17.1	16.5	24.4	37.2%	-0.44	200	30.9	0.82	16.6	18.0	25.5	48.9%	-0.25	
EC ($\mu\text{S/cm}$)	76	2706	415.0	1081	968.5	1620	48.2%	1.14	200	5135	4.46	3281	3448	4164	28.8%	-0.86	
DO (mg/L)	76	13.7	6.83	9.10	8.83	10.2	19.8%	1.16	195	16.2	6.17	9.70	9.61	11.7	19.3%	0.56	
ORP (mV)	76	374.8	-94.1	130.9	142.6	212.2	76.7%	-0.87	199	319.4	-252.8	141.2	159.6	204.5	56.5%	-1.97	

Table 5.3. Basic Statistics for Tributary/Drain Surface Water Samples

Constituent/ Property	N	Maximum	Minimum	Average	Median	Percentile	CV	Skewness	N	Maximum	Minimum	Average	Median	Percentile	CV	Skewness	85th
																	Upstream
C _{Se} ($\mu\text{g/L}$)	27	53.2	4.26	12.8	10.2	19.7	73.9%	3.24	289	51.2	1.28	15.8	14.2	25.8	66.2%	0.89	
C _T ($\mu\text{g/L}$)	22	197.0	7.10	36.3	21.9	54.2	116.4%	3.03	50	138.0	17.0	74.2	81.3	100.3	41.7%	-0.21	
C _{Fe,Tot} (mg/L)	8	59200	243	11660	4815	110000	168%	2.62	213	118000	29	1682	512	1728	490%	13.4	
C _{NH} (mg/L)	27	332.0	27.0	126.4	103.0	194.8	61.7%	1.39	162	647.0	79.0	373.3	368.5	490.6	29.6%	0.14	
C _{Ca} (mg/L)	27	596.0	60.0	221.9	176.0	382.2	59.1%	1.20	162	454.0	0.85	305.4	306.0	362.9	21.4%	-0.83	
C _{Al} (mg/L)	27	179.0	19.0	70.9	57.0	109.8	62.8%	1.26	162	263.0	55.0	141.8	139.0	181.9	25.6%	0.15	
C _K (mg/L)	27	14.0	2.00	4.81	5.00	5.10	46.8%	2.73	162	33.0	6.00	12.4	11.0	15.9	31.8%	1.84	
C _{Na} (mg/L)	26	19.0	0.44	8.28	7.97	13.8	59.8%	0.32	153	23.9	0.44	6.03	5.32	11.1	83.2%	1.26	
C _{CaO} (mg/L)	27	1935	198.0	845.7	672.0	1531	62.9%	0.82	162	2670	168.0	1630	1628	2064	25.5%	-0.30	
C _{Cr} (mg/L)	27	94.0	12.0	42.4	34.0	69.7	56.6%	0.98	162	228.0	42.0	106.5	102.0	135.9	29.5%	0.81	
C _{Co} (mg/L)	27	26.0	1.00	10.2	9.00	17.1	58.4%	0.74	162	48.0	1.00	12.9	15.0	23.0	83.3%	0.58	
C _{CrCo} (mg/L)	27	334.0	124.0	213.1	220.0	250.5	26.9%	0.55	162	462.0	121.0	277.9	273.5	341.9	22.6%	0.19	
C _S (mg/L)	27	0.47	0.07	0.20	0.16	0.29	45.9%	1.22	162	1.17	0.09	0.56	0.55	0.77	37.0%	0.61	
TDS (mg/L)	27	3266	445.6	1538	1292	2700	53.9%	0.77	162	4377	1127	2866	2878	3538	22.8%	-0.28	
pH	26	8.52	6.96	7.91	7.86	8.33	5.1%	-0.86	292	12.3	5.84	8.04	8.04	8.36	7.17%	2.53	
T ($^{\circ}\text{C}$)	27	24.7	2.21	16.4	15.5	22.4	31.3%	-0.64	292	33.3	-0.10	17.0	17.9	25.2	46.1%	-0.26	
EC ($\mu\text{s/cm}$)	27	4326	572.0	1977	1597	3043	49.0%	0.83	292	5803	20.5	3342	3263	4221	24.0%	-0.25	
DO (mg/L)	27	15.5	3.39	9.55	8.96	13.8	31.9%	0.63	276	15.8	0.36	10.1	10.1	13.2	26.7%	-0.31	
ORP (mV)	27	280.6	-97.4	133.0	137.6	229.4	79.8%	-1.09	291	307.6	-246.0	132.1	154.2	193.7	62.4%	-1.88	

5.1.2 Correlation and Regression between Selenium and other Water Quality Constituents

Pearson correlation coefficients (Gauch 2000), r_p , were computed using STATISTICA® (Version 9.0, StatSoft 2009) with the intent of determining relationships between the various sampled constituents and in-situ water quality measurements.

$$r_p = \frac{\sigma_{xy}}{(\sigma_x)(\sigma_y)} \quad \text{Eq. 5.1}$$

These values were computed as variate to variate (X-Y), log variate to variate (Log X-Y and Y-Log X), and log variate to log variate (Log X-Log Y). All relationships that were moderately ($0.3 \leq |r_p| < 0.5$) or strongly ($|r_p| \geq 0.5$) correlated involving C_{Se} , C_U , C_{NO_3} , or C_{SO_4} were reported in Table 5.4. All correlations having $|r_p| \geq 0.3$ were found to be significant with $p < \alpha$ (significance threshold, $\alpha = 0.05$). Table 5.4 show strong correlations between C_{Se} and C_U , C_{NO_3} , and C_B in both study regions. Correlations between all ground water constituents in the Upstream and Downstream Regions are displayed in Appendices E and F, respectively.

It is assumed that C_{Se} and C_U are correlated because each originates from the same primary source (Cretaceous marine shales) in the LARV. This may be beneficial as high C_U values could indicate the likely presence of high C_{Se} values or nearby locations of undiscovered underlying shale deposits. Non-linear least squares regression analysis was used to estimate the predictive relationship between C_{Se} and C_U . The Downstream Study Region was found to have a better “goodness of fit” with $r^2 = 0.44$ with the Upstream Study Region having $r^2 = 0.17$. Figures 5.22 and 5.23 show this data and the fitted relationships for the Upstream and Downstream Study Regions, respectively. Laboratory experiments conducted by Wright (1999) indicate that C_{NO_3} enhances the solubility and mobility of Se by acting as an oxidizing agent. This transforms and

Table 5.4. Moderately and Strongly Correlated Constituents in Upstream and Downstream Ground Water

Upstream Ground Water				Downstream Ground Water			
Variate X	Variate Y	Correlation Relationship	r_P	Variate X	Variate Y	Correlation Relationship	r_P
C_{Se}	EC	Log X-Log Y	0.35	C_{Se}	EC	Log X-Y	0.48
	C_U	Log X-Log Y	0.52	C_U	X-Y	0.73	
	C_{Na}	X-Log Y	0.43	C_{Na}	Log X-Log Y	0.50	
	C_{Mg}	Log X-Log Y	0.42	C_{Ca}	Log X-Y	0.31	
	C_{NO_3}	X-Y	0.69	C_{Mg}	Log X-Log Y	0.49	
	C_{SO_4}	Log X-Log Y	0.41	C_{NO_3}	X-Y	0.97	
	C_{Cl}	X-Log Y	0.42	C_{SO_4}	Log X-Y	0.50	
	C_B	X-Y	0.50	C_{Cl}	Log X-Log Y	0.48	
	TDS	Log X-Log Y	0.40	C_B	Log X-Log Y	0.49	
				TDS	Log X-Log Y	0.51	
C_U	EC	X-Y	0.68	C_U	EC	X-Y	0.67
	C_{Na}	X-Y	0.88	C_{Na}	X-Y	0.82	
	C_K	Log X-Log Y	-0.34	C_{Ca}	Log X-Log Y	0.59	
	C_{Ca}	Log X-Log Y	0.63	C_{Mg}	X-Y	0.89	
	C_{Mg}	X-Y	0.87	C_{SO_4}	X-Y	0.85	
	C_{SO_4}	X-Y	0.89	C_{Cl}	X-Y	0.75	
	C_{Cl}	X-Y	0.57	C_{CO_3}	Log X-Log Y	0.33	
	C_{HCO_3}	X-Y	0.55	C_{HCO_3}	X-Log Y	0.30	
	C_B	X-Log Y	0.67	C_B	X-Y	0.85	
	TDS	X-Y	0.90	TDS	X-Y	0.84	
C_{NO_3}	EC	X-Y	0.33	C_{NO_3}	EC	X-Y	0.38
	C_{Na}	X-Log Y	0.33	C_{Fe}	Log X-Log Y	-0.44	
	C_{SO_4}	X-Log Y	0.30	C_{Na}	Log X-Log Y	0.31	
	C_{Cl}	X-Log Y	0.31	C_{Mg}	Log X-Log Y	0.32	
	C_B	X-Log Y	0.31	C_{Cl}	Log X-Log Y	0.35	
	TDS	X-Log Y	0.31	C_{HCO_3}	X-Log Y	-0.30	
				TDS	Log X-Log Y	0.34	
C_{SO_4}	EC	X-Y	0.79	C_{SO_4}	EC	X-Y	0.80
	C_{Na}	X-Y	0.99	C_{Na}	X-Y	0.91	
	C_{Ca}	Log X-Log Y	0.81	C_{Ca}	Log X-Y	0.68	
	C_{Mg}	X-Y	0.97	C_{Mg}	X-Y	0.91	
	C_{Cl}	Log X-Log Y	0.73	C_{Cl}	X-Log Y	0.79	
	C_{HCO_3}	X-Y	0.62	C_{HCO_3}	X-Y	0.38	
	C_B	Log X-Log Y	0.78	C_B	X-Log Y	0.74	
	TDS	X-Y	1.00	TDS	X-Y	0.95	

maintains Se in the highly soluble form of selenate. The relationship between C_{Se} and C_{NO_3} is significant because nitrogen fertilizer application, an anthropogenic practice that may be regulated, induces nitrification which seems to contribute to high Se concentrations. Shown in Figures 5.24 and 5.25, least squares regression analysis was used to find non-linear best fit equations for this relationship in both study regions. Similar patterns are seen between Upstream and Downstream plots for each constituent. Figures 5.24 and 5.25 also illustrate the higher correlation between C_{NO_3} and C_{Se} than C_U and C_{Se} .

The extremely high correlations ($|r_p| \geq 0.9$) between C_{SO_4} and TDS supports the suggestion that TDS is primarily composed of the SO_4 anion. C_{SO_4} is also extremely highly correlated with C_{Na} ($|r_p| \geq 0.9$) and very highly correlated ($|r_p| \geq 0.79$) with EC in both study regions.

Table 5.4 shows that C_B is strongly correlated with C_{Se} , C_U , and C_{SO_4} in both study regions. Hudak (2004) found a strong and significant Spearman correlation coefficient of 0.58 between C_B and C_{Se} when sampling ground water from the Gulf Coast Aquifer System in Texas, USA. This strong correlation between C_{Se} and C_B may indicate that each constituent has similar sources and is subject to similar dissolution and mobilization processes.

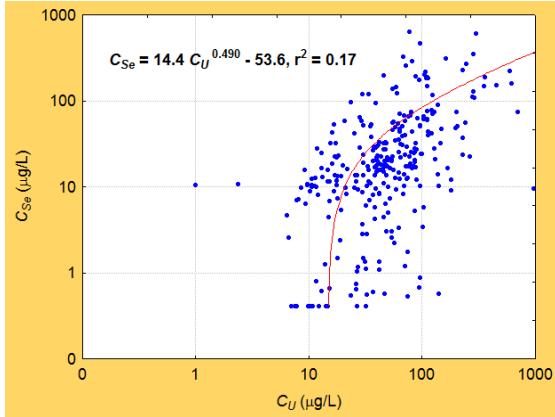


Figure 5.22. Regression plot of C_{Se} vs. C_U in the ground water of the Upstream Study Region

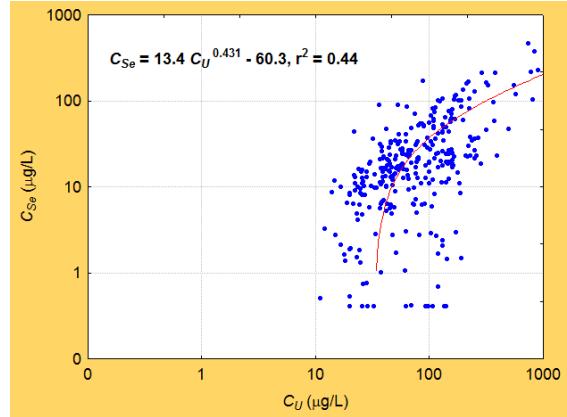


Figure 5.23. Regression plot of C_{Se} vs. C_U in the ground water of the Downstream Study Region

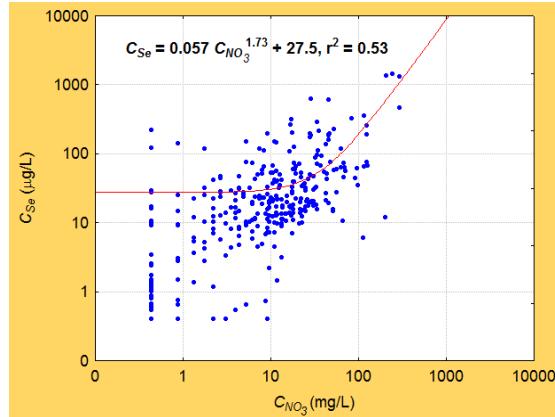


Figure 5.24. Regression plot of C_{Se} vs. C_{NO_3} in the ground water of the Upstream Study Region

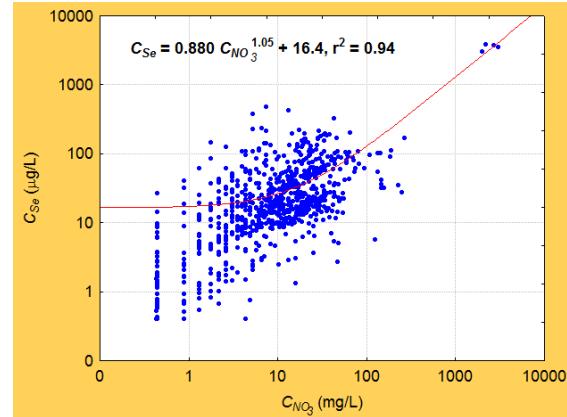


Figure 5.25. Regression plot of C_{Se} vs. C_{NO_3} in the ground water of the Downstream Study Region

5.1.3 Temporal and Spatial Patterns of Constituent Concentrations

Computed statistics, box and whisker plots, and contour plots reveal the substantial temporal and spatial variability among sampled constituent concentrations in the LARV. Figures 5.26 and 5.27 show box and whisker plots that provide medians, 15-85th percentile ranges, and outliers of C_{Se} over time in the routinely-monitored ground water locations of the Upstream and Downstream Study Regions, respectively. Median ground water C_{Se} seems to decrease in the fall in both study regions. This may be caused by dilution associated with ground water recharge from over-irrigation and canal seepage throughout the growing season. Figure 5.28 is a box and

whisker plot of C_{Se} at each of the routinely-monitored Arkansas River locations in the Downstream Study Region. Sampling point identification numbers in this plot increase in the downstream direction along the river. Median C_{Se} in the river seems to be increasing downstream. This is most likely due to river water being continually diverted for irrigation and returning to the river as return flows after dissolution, mobilization, and evapoconcentration of Se.

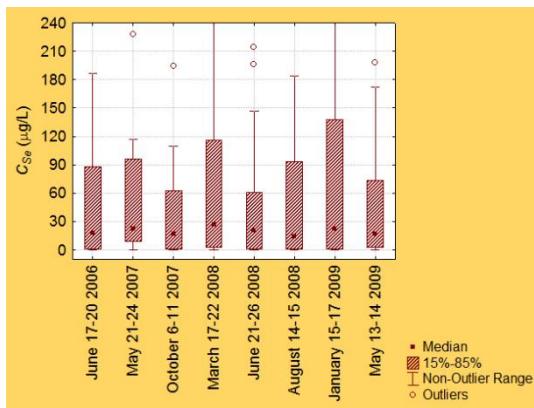


Figure 5.26. Box and whisker plot of C_{Se} over time in routinely-monitored ground water of the Upstream Study Region

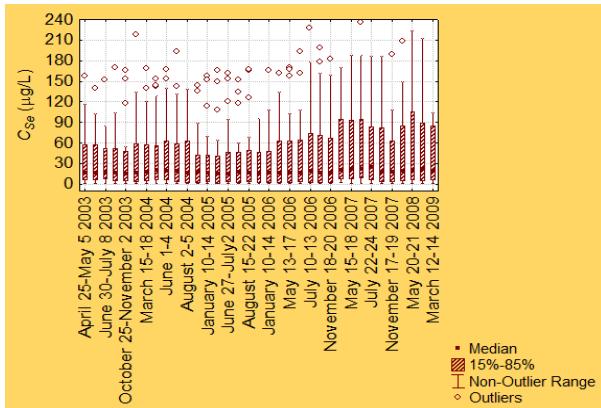


Figure 5.27. Box and whisker plot of C_{Se} over time in routinely-monitored ground water of the Downstream Study Region

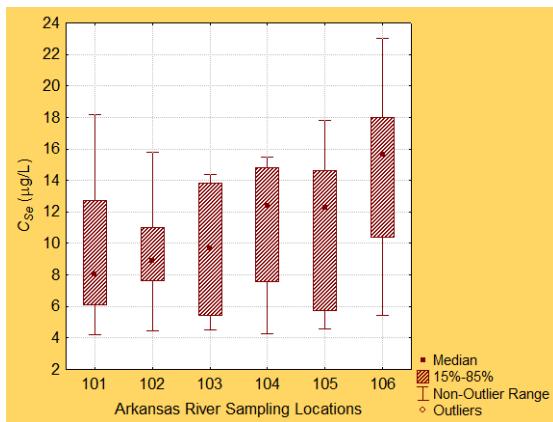


Figure 5.28. Box and whisker plot of C_{Se} in the routinely-monitored Arkansas River locations of the Downstream Study Region

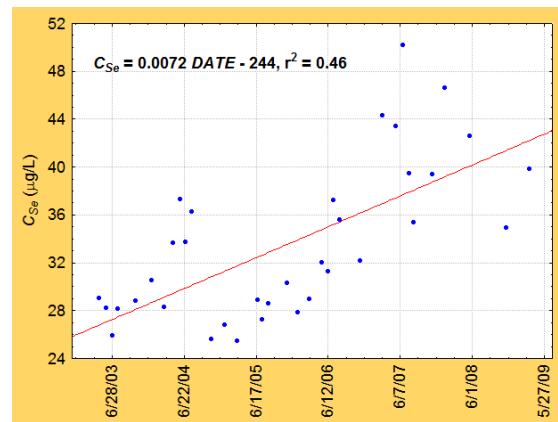


Figure 5.29. Time series plot of average C_{Se} in the Downstream Study Region

Figure 5.29 plots average C_{Se} concentration of routine ground water locations per each sampling event and with a statistically significant ($\alpha = 0.05$) least squares best fit line though these points. This plot suggests that C_{Se} has been increasing in the ground water of the LARV over the six-year life of the project.

Temporal variations in C_{Se} and C_{NO_3} were plotted for selected ground water monitoring wells.

Figures 5.30 through 5.33 show time series plots for Upstream wells 1, 11, 12, and 22 while plots for Downstream wells 301, 334, 365, and 371 are presented in Figures 5.34 through 5.37. C_{Se} tends to directly relate to C_{NO_3} over time. This is expected, as NO_3 has been found to oxidize other forms of Se into its most soluble form of selenate and to inhibit subsequent reduction. A closer examination of the plots reveals that there does not seem to be a time-lagged correlation between C_{Se} and C_{NO_3} . There are several possible causes for imperfections in correspondence between C_{Se} and C_{NO_3} seen in these time series plots. If all available Se has been oxidized into selenate, an increase in C_{NO_3} would not further increase C_{Se} . Other oxidizing agents such as DO or SO_4^{2-} may be present, increasing C_{Se} without affecting C_{NO_3} . Several other factors such as microbial activity, organic carbon content, and/or pH levels also add layers of complexity to the relationship between C_{Se} and C_{NO_3} .

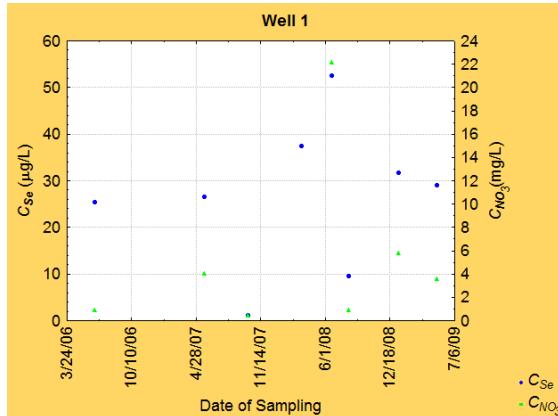


Figure 5.30. Time series plot of C_{Se} and C_{NO_3} data from Upstream well 1

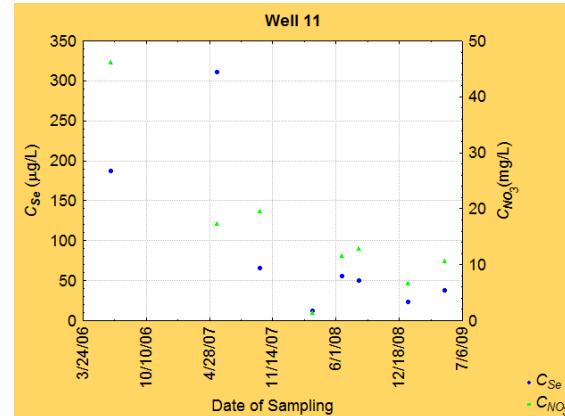


Figure 5.31. Time series plot of C_{Se} and C_{NO_3} data from Upstream well 11

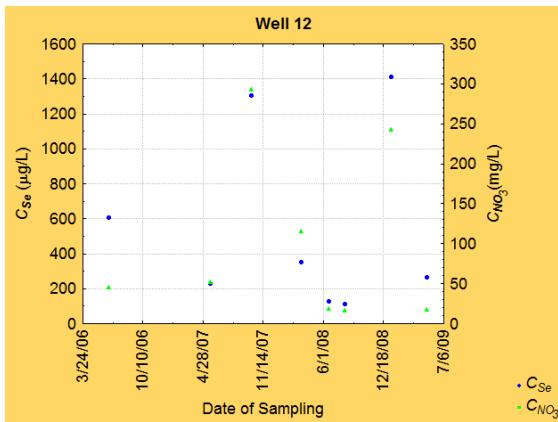


Figure 5.32. Time series plot of C_{Se} and C_{NO_3} data from Upstream well 12

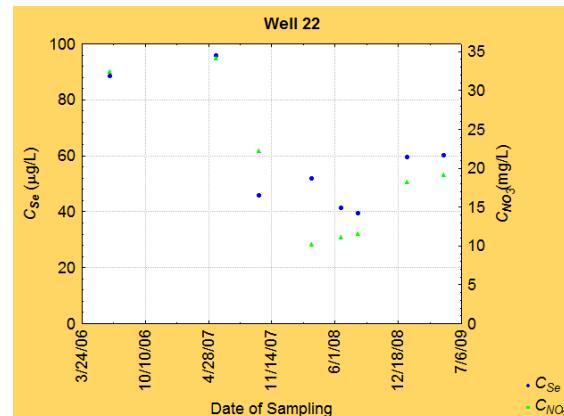


Figure 5.33. Time series plot of C_{Se} and C_{NO_3} data from Upstream well 22

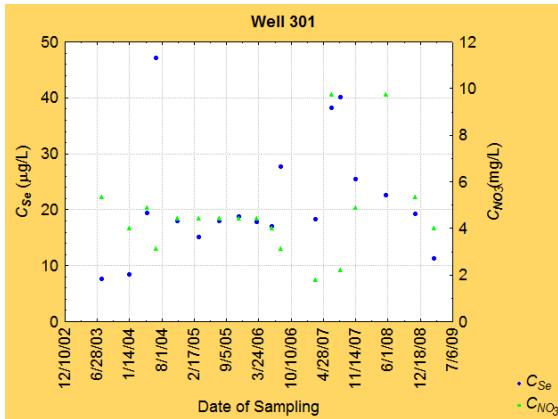


Figure 5.34. Time series plot of C_{Se} and C_{NO_3} data from Downstream well 301

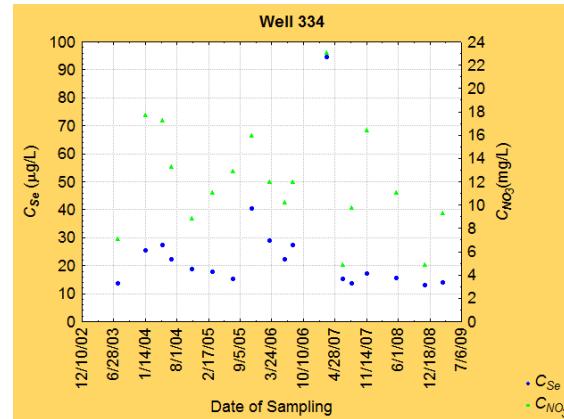


Figure 5.35. Time series plot of C_{Se} and C_{NO_3} data from Downstream well 334

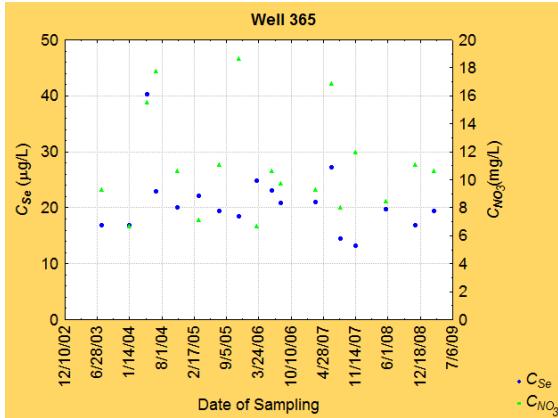


Figure 5.36. Time series plot of C_{Se} and C_{NO_3} data from Downstream well 365

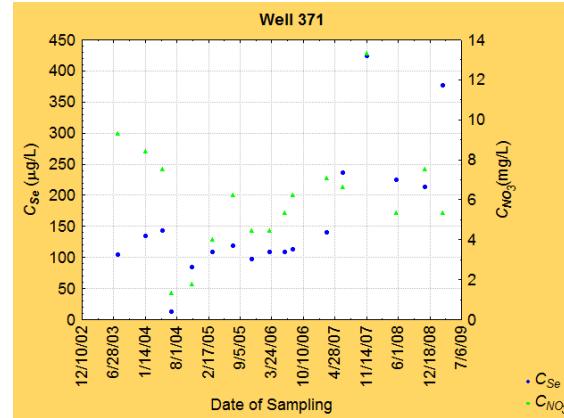


Figure 5.37. Time series plot of C_{Se} and C_{NO_3} data from Downstream well 371

Coefficients of variation, CVs, computed over all routine ground water C_{Se} values were 266% and 140% for the Upstream and Downstream Study Regions, respectively. The spatial coefficient of variation, CVs, for each sampling event was also computed. The Upstream Study Region's CV values ranged between 141% and 339% while for the Downstream Study Region's they ranged between 105% and 188%. The larger CV values found in the Upstream Study Region are likely due to the larger numbers of ground water samples containing high C_{Se} values found in this region.

These high CV values, as well as contour plots of ground water concentrations generated using the "natural neighbor" interpolation function of GMSTM (BYU 2002) of C_{Se} , C_U , and C_{NO_3} , reveal the substantial spatial variability in both regions between August 2007 and May 2009. While the natural neighbor method displays exact values at imputed locations it uses a Thiessen/Voroni technique to estimate unknown locations based upon nodal influence (BYU 2002). Figures 5.38 through 5.54 show contour plots for this period for the Upstream Study Region while Figures 5.55 though 5.69 show contour plots for the Downstream Study Region. Each page containing contour plots represents an individual sampling event. Wells 12, 20, 21, and 22 on the western edge of the Upstream Study Region have consistently yielded high C_{Se} , C_U , and C_{NO_3} values throughout this period. Also, there seems to be a second hotspot in the vicinity of wells 83 and 84. There are two consistent hotspots located in the northwest area of the Downstream Study Region. The more central spot is near wells 371 and 372 while the further west location is near wells 387, 392, and 393. Correlations between constituents are visually represented in these contour plots by high C_{Se} , C_U , and C_{NO_3} values being found in similar locations. Contour plots for all sampling periods over the life of the project may be seen in Appendix G.

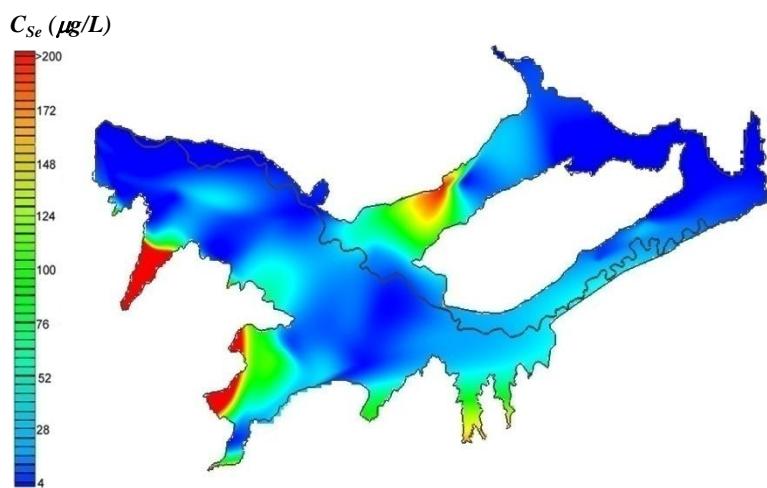


Figure 5.38. Contour plot of C_{Se} from samples collected during October 6-11, 2007 in the Upstream Study Region.

No C_U Data
During this Event

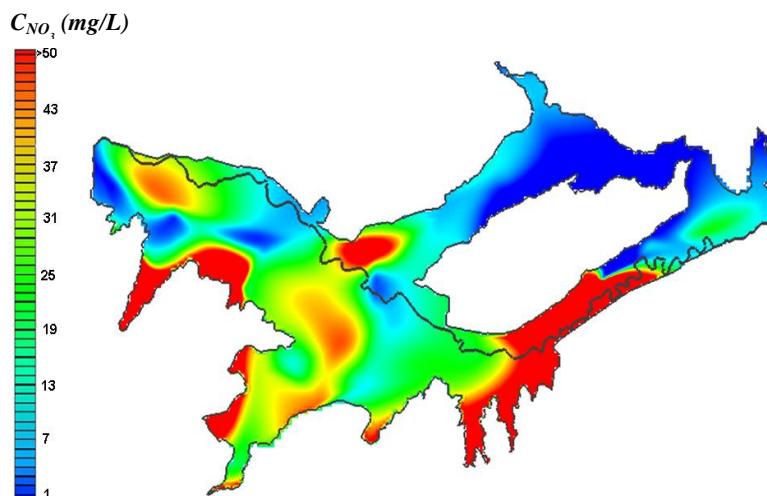


Figure 5.39. Contour plot of C_{NO_3} from samples collected during October 6-11, 2007 in the Upstream Study Region.

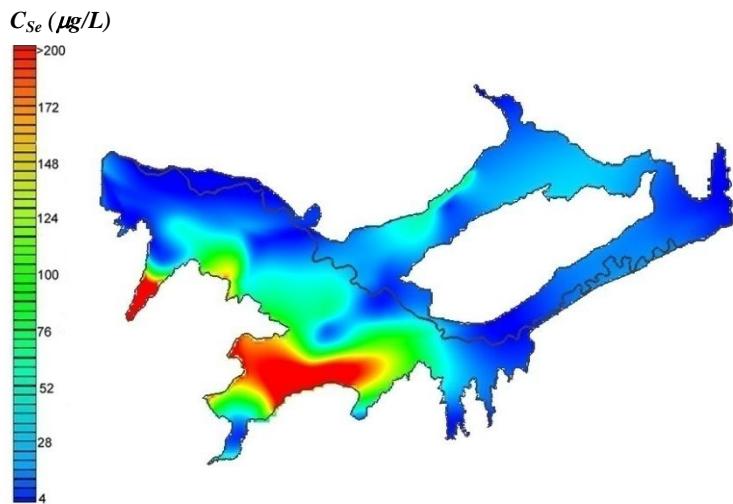


Figure 5.40. Contour plot of C_{Se} from samples collected during March 17-22, 2008 in the Upstream Study Region.

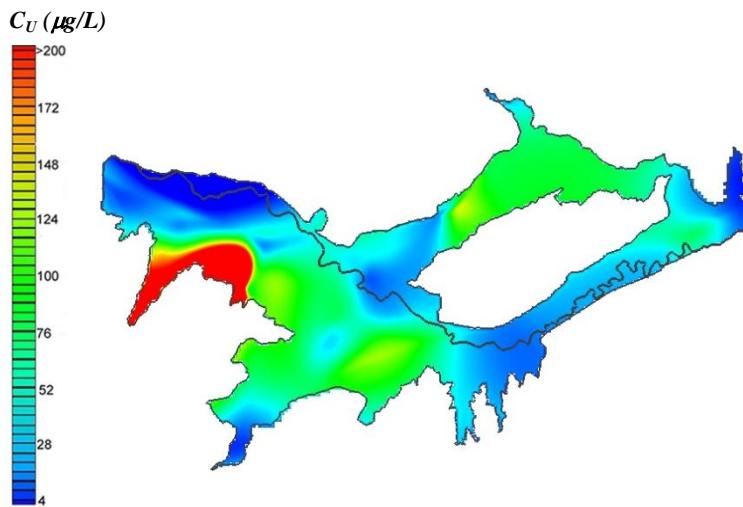


Figure 5.41. Contour plot of C_U from samples collected during March 17-22, 2008 in the Upstream Study Region.

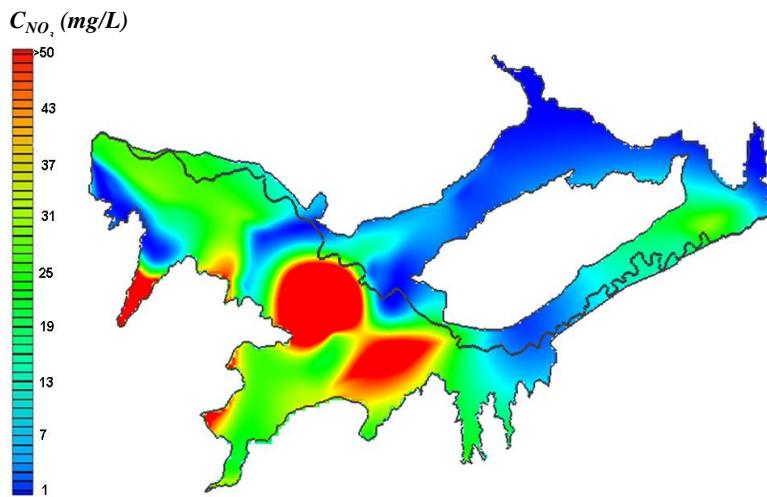


Figure 5.42. Contour plot of C_{NO_3} from samples collected during March 17-22, 2008 in the Upstream Study Region.

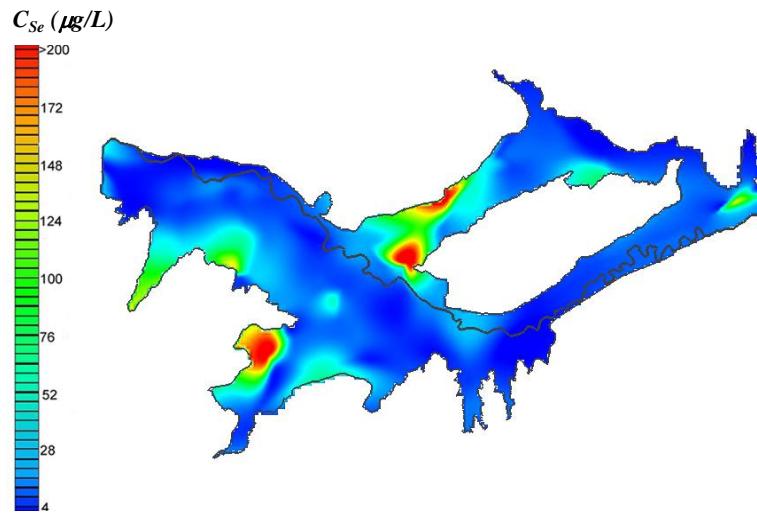


Figure 5.43. Contour plot of C_{Se} from samples collected during June 21-26, 2008 in the Upstream Study Region.

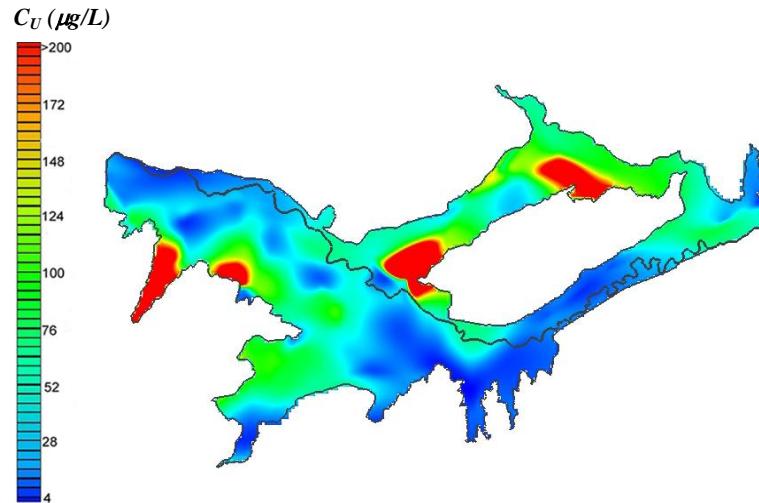


Figure 5.44. Contour plot of C_U from samples collected during June 21-26, 2008 in the Upstream Study Region.

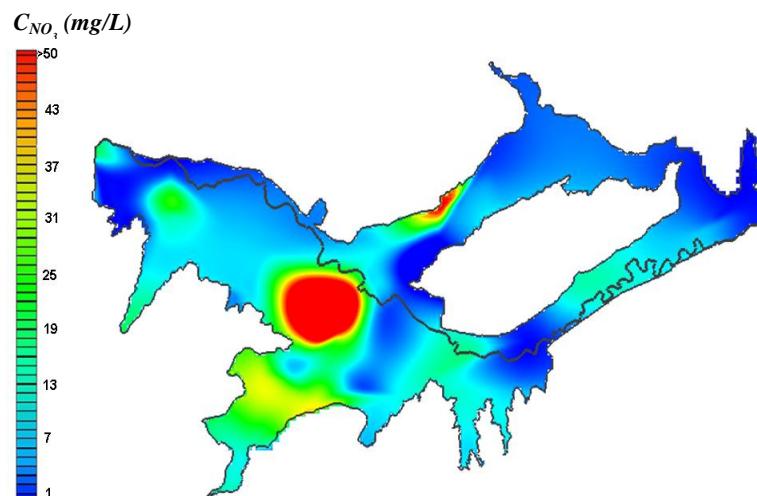


Figure 5.45. Contour plot of C_{NO_3} from samples collected during June 21-26, 2008 in the Upstream Study Region.

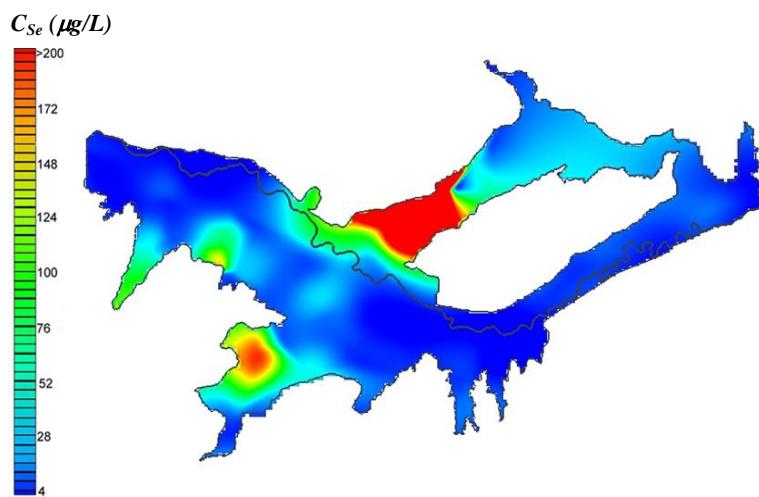


Figure 5.46. Contour plot of C_{Se} from samples collected during August 14-15, 2008 in the Upstream Study Region.

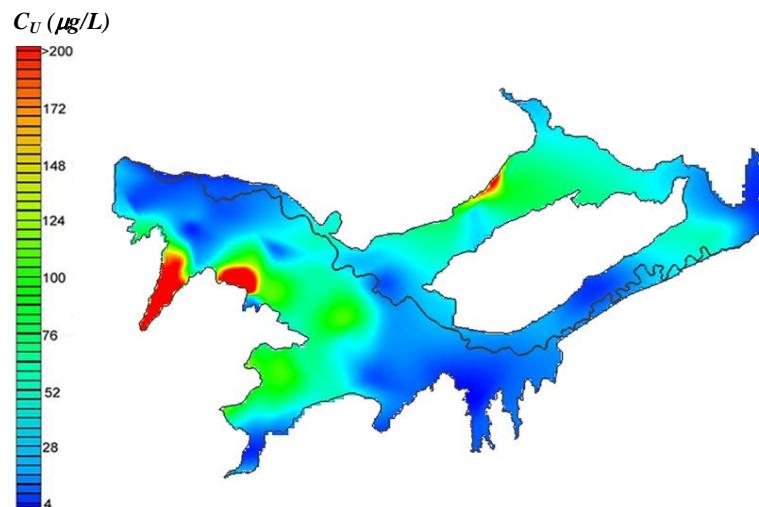


Figure 5.47. Contour plot of C_U from samples collected during August 14-15, 2008 in the Upstream Study Region.

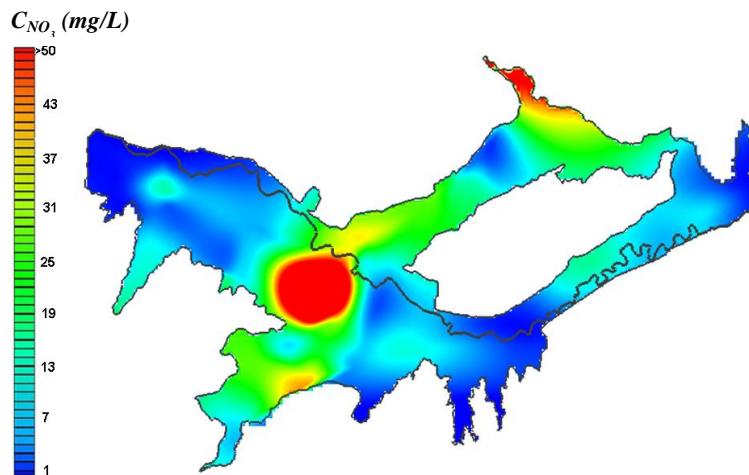


Figure 5.48. Contour plot of C_{NO_3} from samples collected during August 14-15, 2008 in the Upstream Study Region.

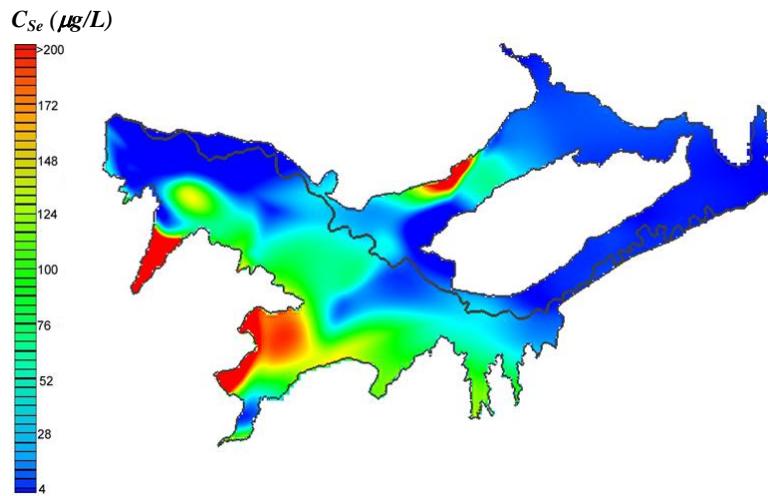


Figure 5.49. Contour plot of C_{Se} from samples collected during January 15-17, 2009 in the Upstream Study Region.

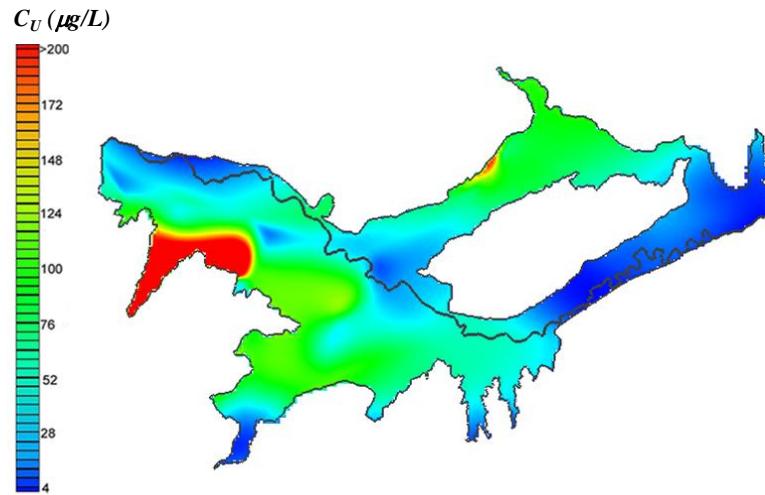


Figure 5.50. Contour plot of C_U from samples collected during January 15-17, 2009 in the Upstream Study Region.

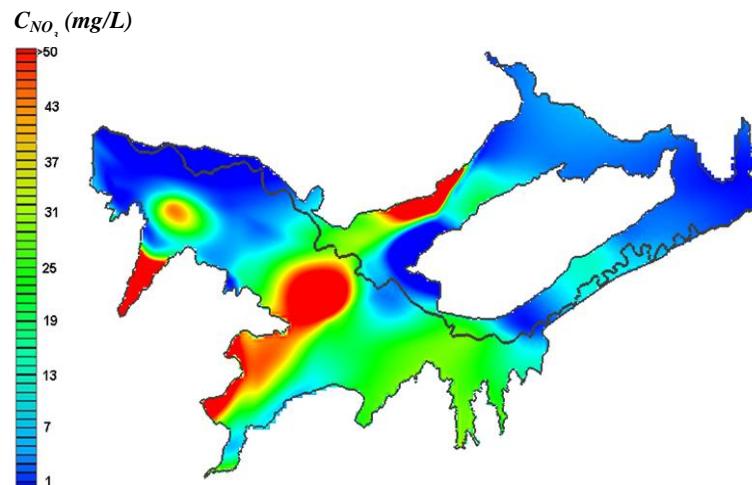


Figure 5.51. Contour plot of C_{NO_3} from samples collected during January 15-17, 2009 in the Upstream Study Region.

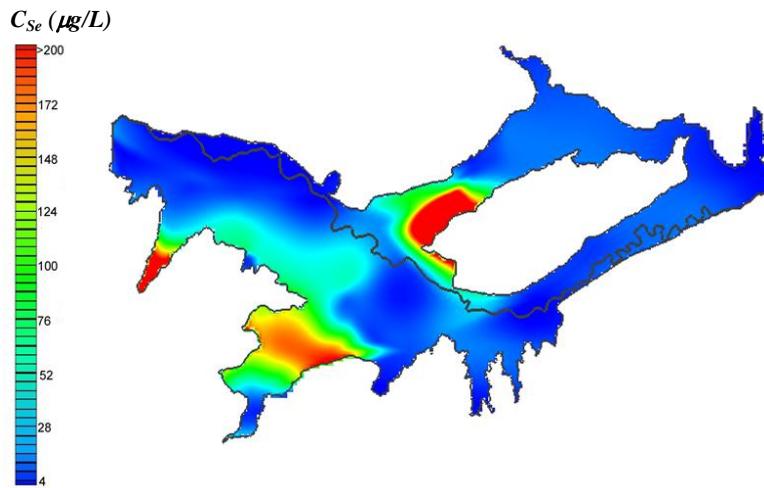


Figure 5.52. Contour plot of C_{Se} from samples collected during May 13-14, 2009 in the Upstream Study Region.

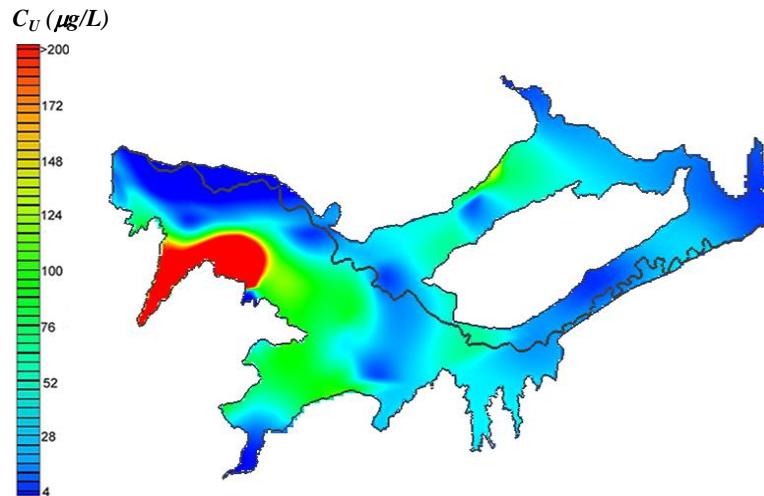


Figure 5.53. Contour plot of C_U from samples collected during May 13-14, 2009 in the Upstream Study Region.

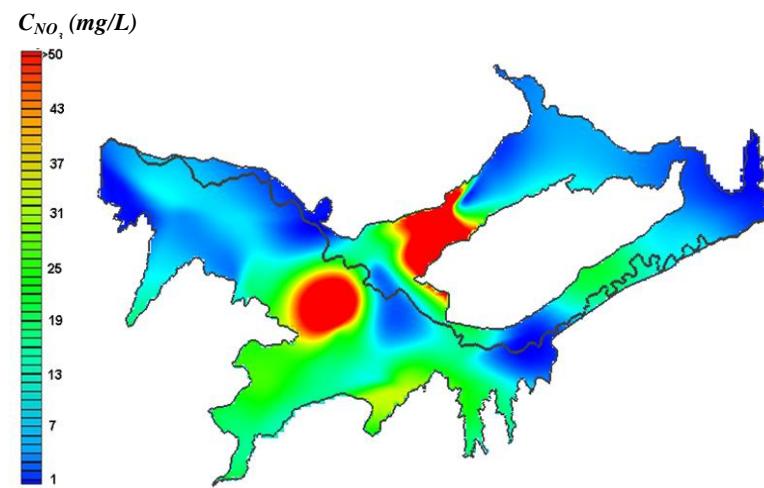


Figure 5.54. Contour plot of C_{NO_3} from samples collected during May 13-14, 2009 in the Upstream Study Region.

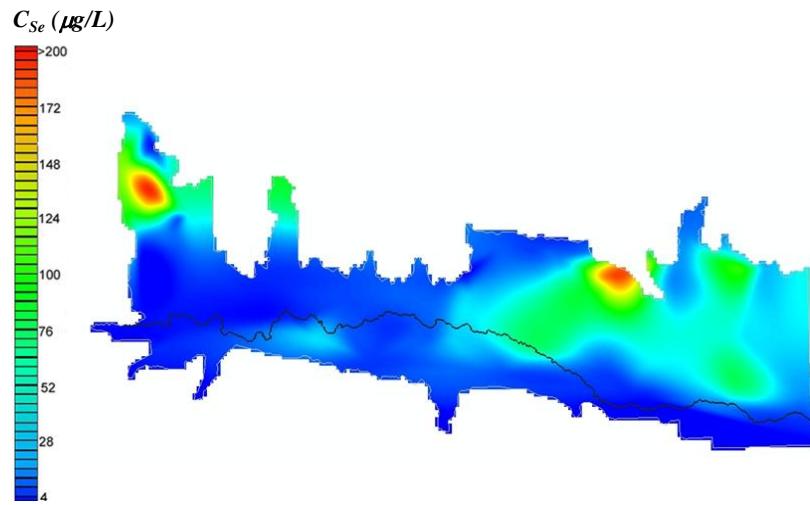


Figure 5.55. Contour plot of C_{Se} from samples collected during August 14-15, 2007 in the Downstream Study Region.

No C_U Data
During this Event

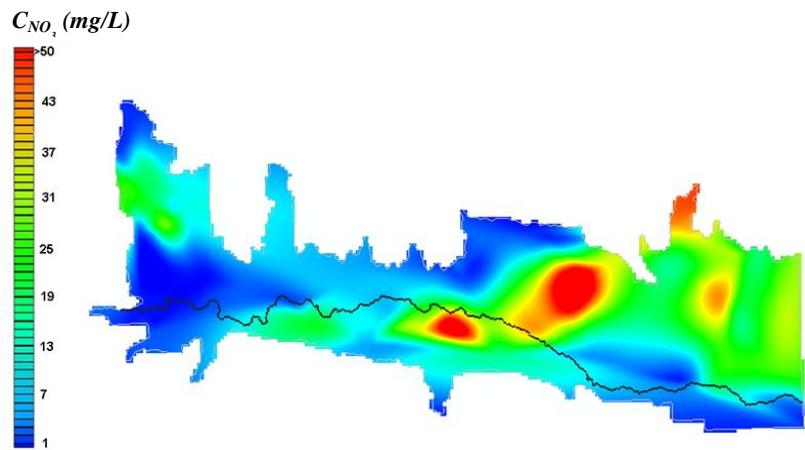


Figure 5.56. Contour plot of C_{NO_3} from samples collected during August 14-15, 2007 in the Downstream Study Region.

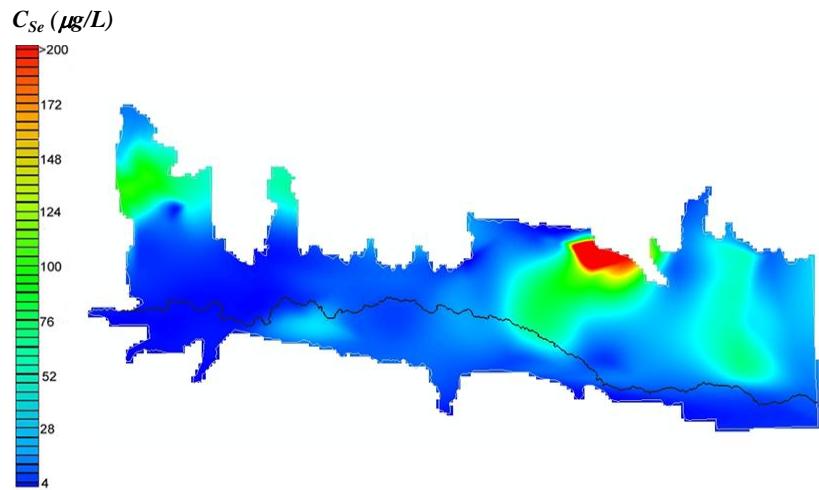


Figure 5.57. Contour plot of C_{Se} from samples collected during November 17-19, 2007 in the Downstream Study Region.

No C_U Data
During this Event

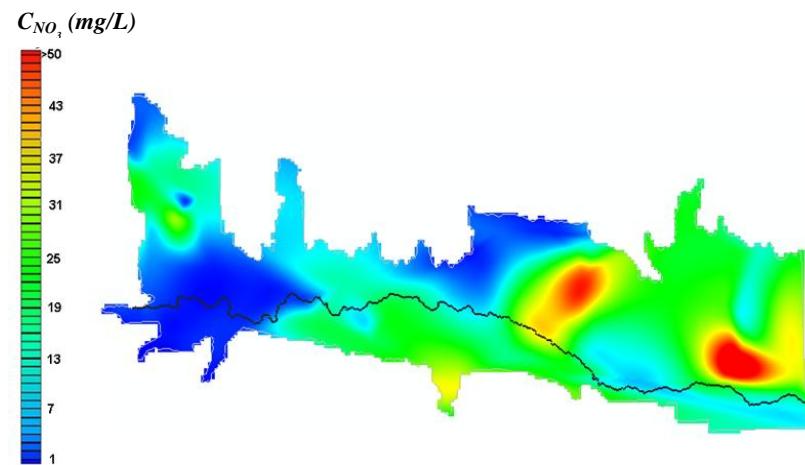


Figure 5.58. Contour plot of C_{NO_3} from samples collected during November 17-19, 2007 in the Downstream Study Region.

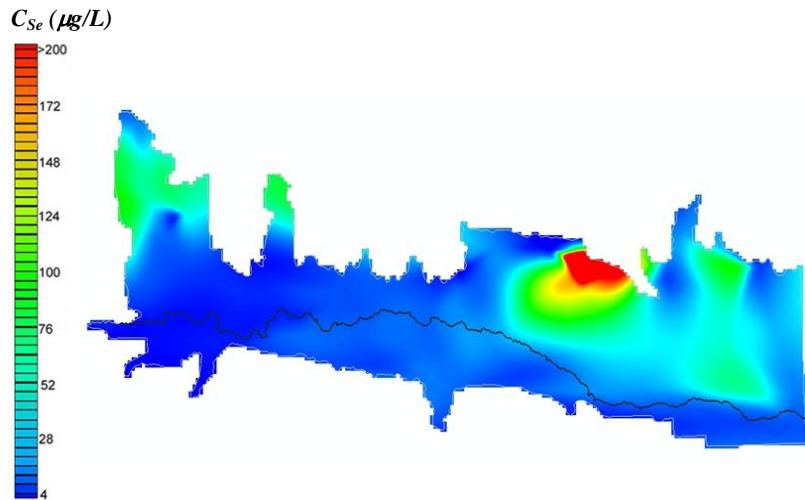


Figure 5.59. Contour plot of C_{Se} from samples collected during January 15-17, 2008 in the Downstream Study Region.

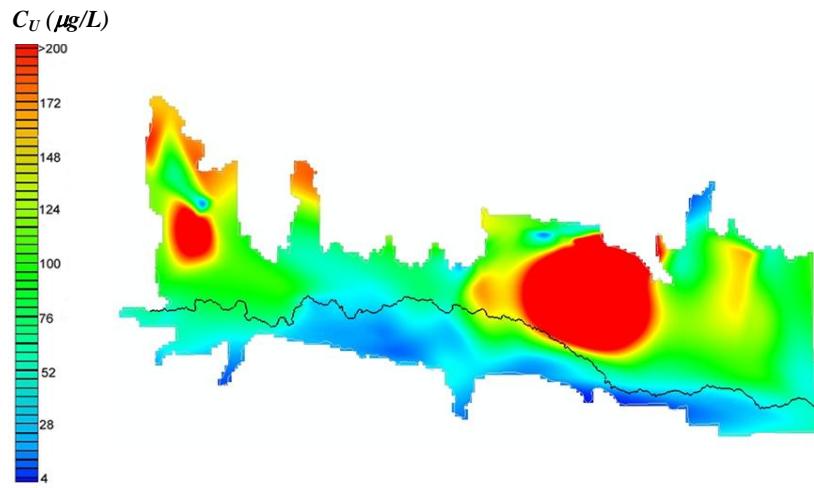


Figure 5.60. Contour plot of C_U from samples collected during January 15-17, 2008 in the Downstream Study Region.

No C_{NO_3} Data
During this Event

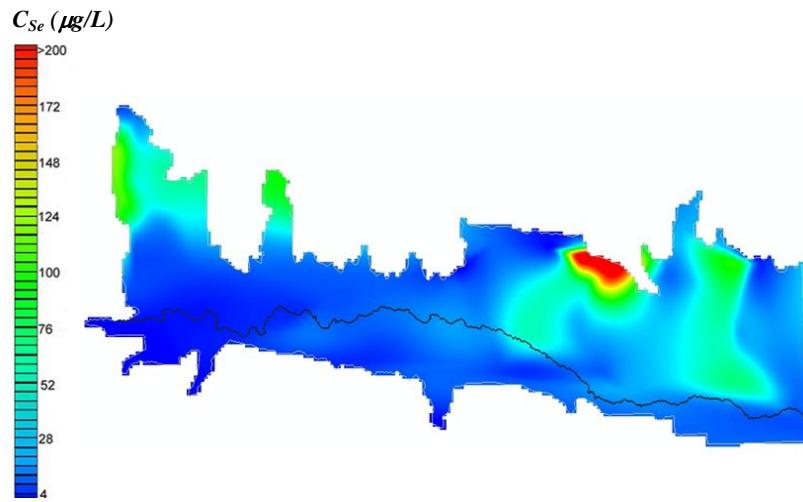


Figure 5.61. Contour plot of C_{Se} from samples collected during May 20-23, 2008 in the Downstream Study Region.

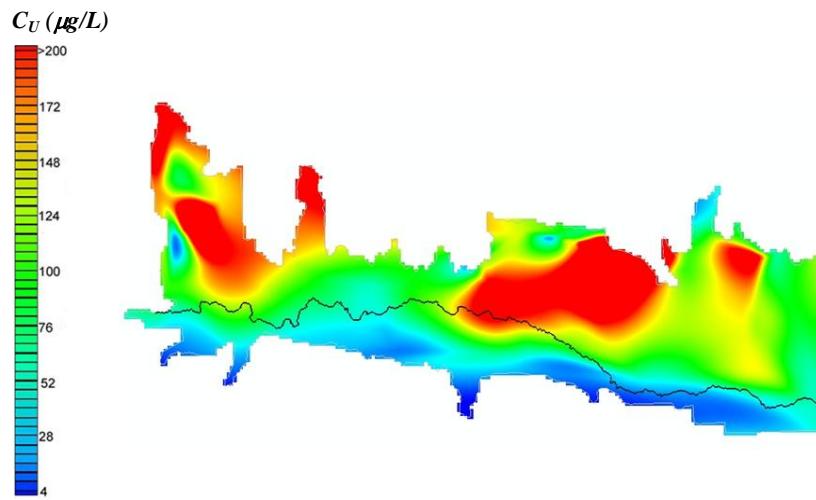


Figure 5.62. Contour plot of C_U from samples collected during May 20-23, 2008 in the Downstream Study Region.

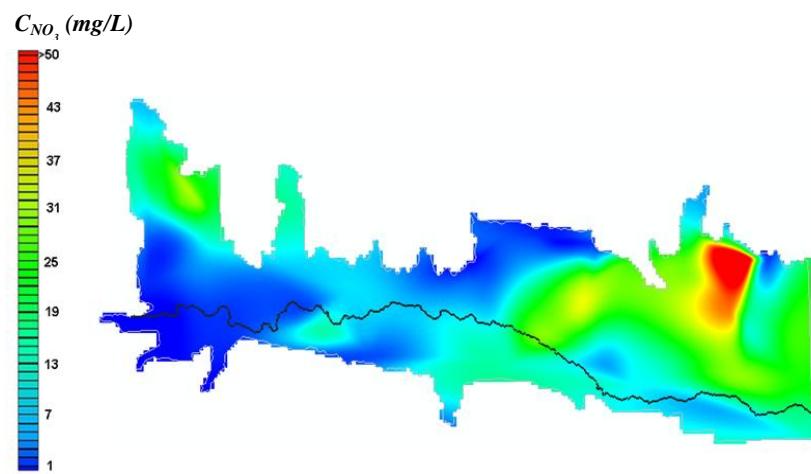


Figure 5.63. Contour plot of C_{NO_3} from samples collected during May 20-23, 2008 in the Downstream Study Region.

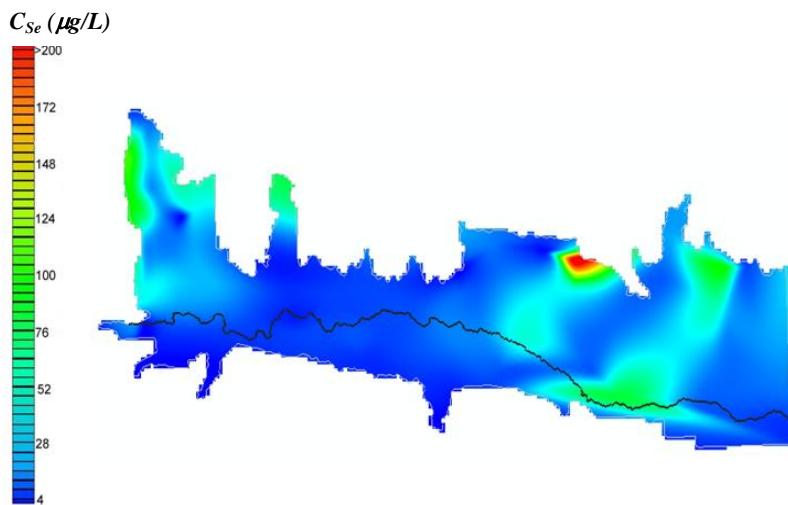


Figure 5.64. Contour plot of C_{Se} from samples collected during November 20-21, 2008 in the Downstream Study Region.

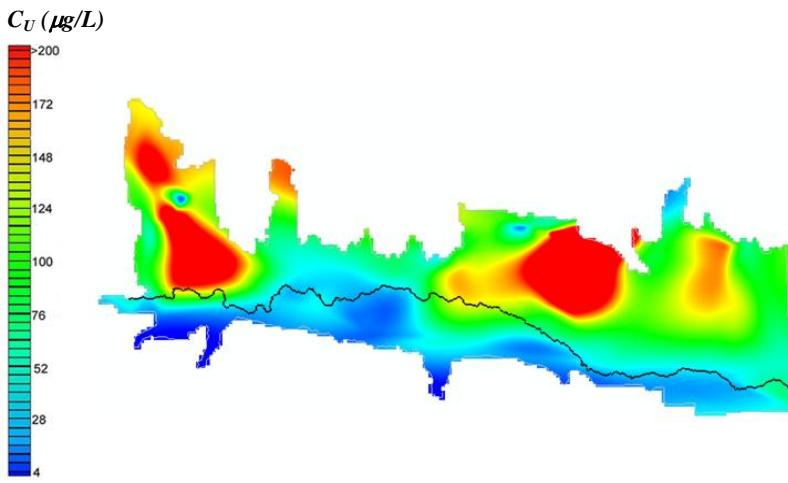


Figure 5.65. Contour plot of C_U from samples collected during November 20-21, 2008 in the Downstream Study Region.

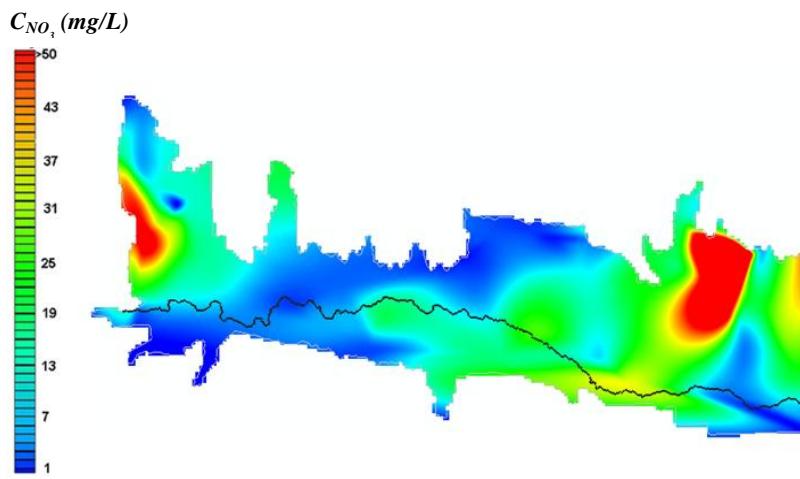


Figure 5.66. Contour plot of C_{NO_3} from samples collected during November 20-21, 2008 in the Downstream Study Region.

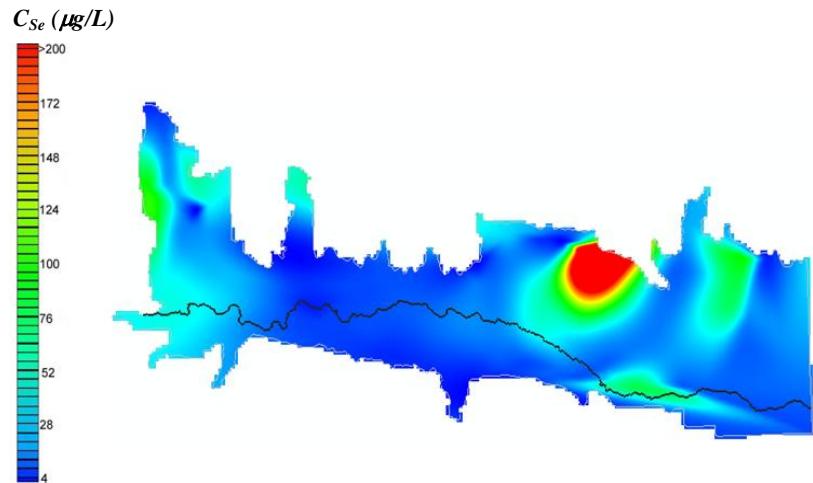


Figure 5.67. Contour plot of C_{Se} from samples collected during March 12-14, 2009 in the Downstream Study Region.

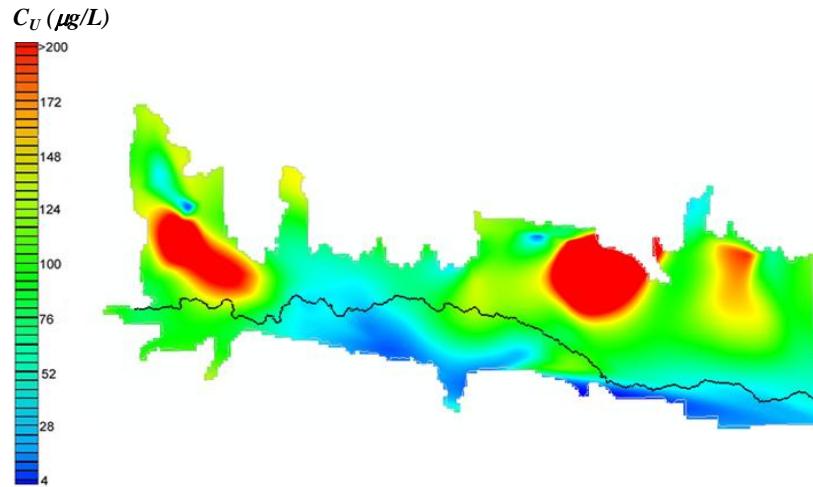


Figure 5.68. Contour plot of C_U from samples collected during March 12-14, 2009 in the Downstream Study Region.

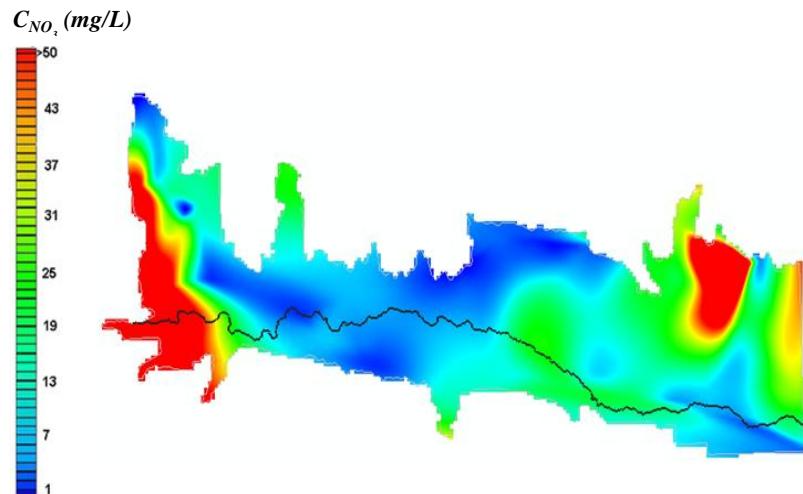


Figure 5.69. Contour plot of C_{NO_3} from samples collected during March 12-14, 2009 in the Downstream Study Region.

A spatial correlation analysis was performed on the Upstream and Downstream ground water data sets to determine how strongly spatial proximity affected similarity between constituent concentrations. It was expected that relatively closely-spaced monitoring well sites would display high correlation between sampled constituent concentrations and that this correlation would decrease as spacing between monitoring sites increased.

A computer program was written using MATLAB® (Version R2008b, The Mathworks 2008) in an attempt to analyze spatial correlations. First, a list of all cases of distances separating monitoring wells was generated. For example, if a study region had four monitoring wells then the region would have six cases of well separation distance; well 1 to well 2, 1 to 3, 1 to 4, 2 to 3, 2 to 4, and 3 to 4. The Upstream and Downstream Study Regions had 4,851 and 3,655 cases of separation distance, respectively. Next, a distance interval was specified to divide the separation distance data into classes. The program would then determine the number of cases in each distance interval, and compute the Pearson correlation coefficient for all cases in that interval along with the associated significance value for each interval. For example, if a distance interval of 300 m was chosen for analyzing a data set with a minimum well separation distance of 100 m and a maximum well separation distance of 1000 m, the data cases were divided into 3 classes: 100-400 m, 400-700 m, and 700-1000 m. The challenge was to find an interval that was large enough to include an ample number of cases for computing statistically significant correlation values yet small enough for higher resolution. Ground water samples over a large area tend to vary greatly as seen in the previously referenced contour plots.

Unfortunately, the monitoring wells in the two study regions were found to be too widely spaced to show clear results. The minimum distances between wells were 391.6 m and 488.3 m in the Upstream and Downstream Study Regions, respectively, with each region having less than 10 cases of separation distances between wells less than 1 km. This resulted in too few wells spaced within a close enough proximity to indicate a significant correlation between constituents. Hence, the analysis suggested that the correlation length, the maximum spatial distance in which same constituents measured from different locations are significantly correlated, for the sampled constituents was less than 1 km.

5.2 Assessing Selenium Mobilization due to Nitrate and Dissolved Oxygen

5.2.1 Rationale for Assessment of Se Mobilization

It is known that Se needs oxidizing conditions to transform into and remain in its soluble forms of selenite and selenate. This fact, coupled with the theory that underlying marine shales are a primary source of Se contamination (Presser 1994) within the LARV gives rise to the following questions:

1. Does our data set provide evidence of Se mobilization when oxygen-rich ground water comes into contact with underlying shale deposits?
2. How much of a role does NO_3 play in providing an oxidizing, hence mobilizing, environment for Se?

If the presence of NO_3 seems to greatly affect the mobilization and occurrence of dissolved Se, policies for managing N fertilizer application especially in proximity to underlying shale deposits, may substantially improve the LARV's ground and surface water quality.

5.2.2 Estimating Se-Bearing Formation Locations

Identified underlying shale locations, or deposits of marine shale within about 5 meters of the soil surface (Watts 2009), were digitized from preexisting USGS maps (Sharps 1976, Scott 1968, Scott et al. 1978) and added as a layer upon maps of the study regions as shown in Figures 5.70 and 5.71. The Upstream Study Region seems to have vastly greater shale deposits than the Downstream Study Region. This may account for the higher average values of C_{Se} in ground water in the Upstream Study Region and was investigated as described in the following sections.

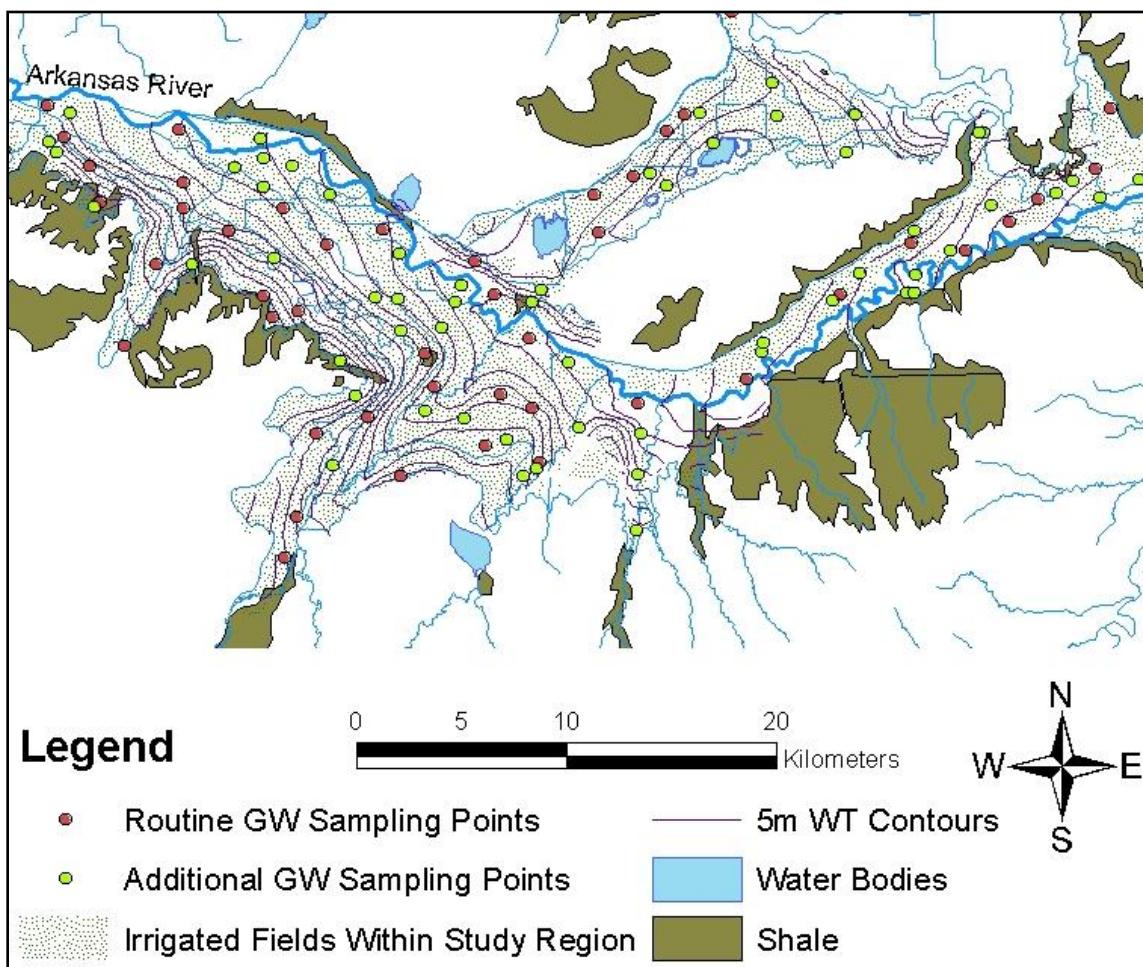


Figure 5.70. Identified Shale Locations and Average Water Table Contours in the Upstream Study Region.

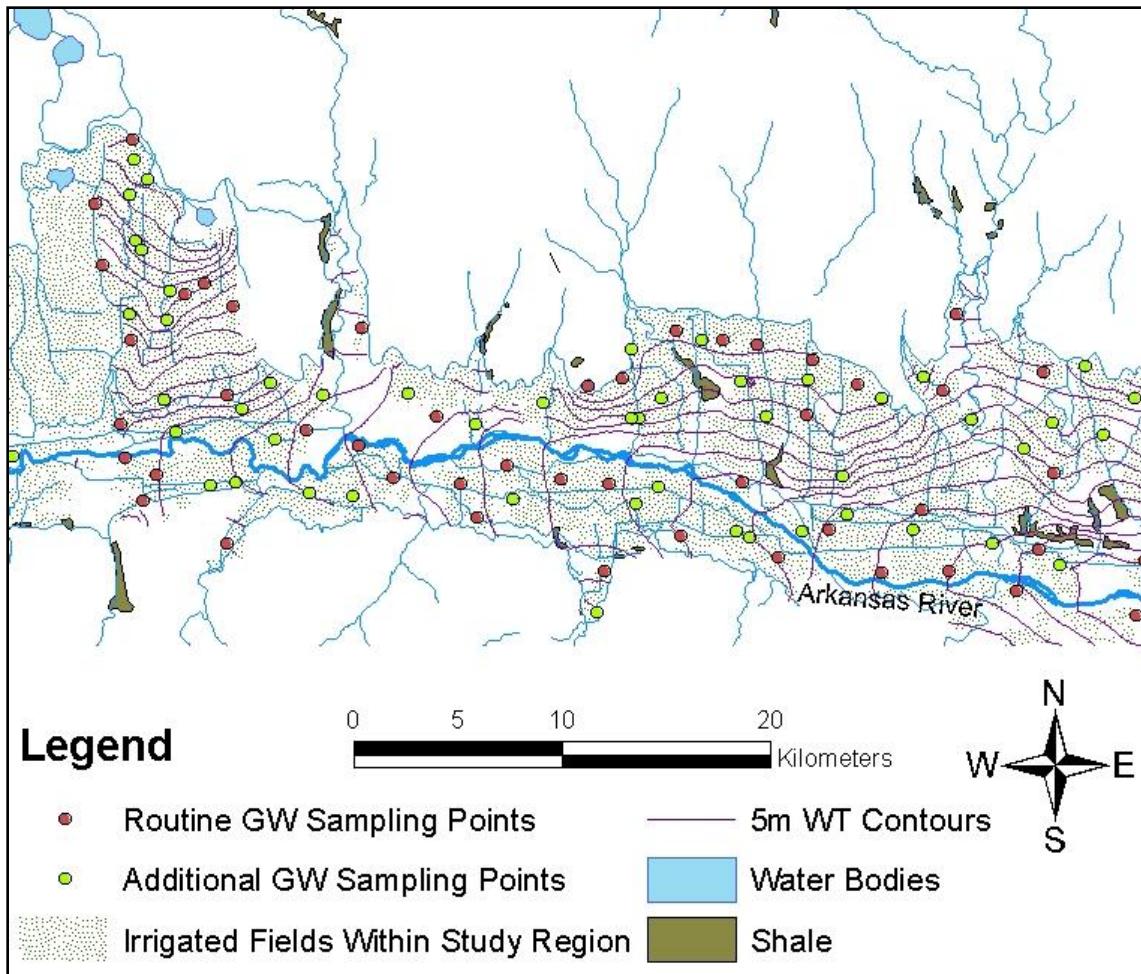


Figure 5.71. Identified Shale Locations and Average Water Table Contours in the Downstream Study Region.

5.2.3 Estimating Ground Water Flow Directions

Average ground water flow directions within the study regions were estimated as perpendicular to contours of water table elevations calculated using a calibrated finite-difference ground water flow model of the regions similar to that described by Burkhalter and Gates (2005). Contours of average water table elevations, calculated by the model and plotted in Figures 5.70 and 5.71, indicate that the direction of ground water flow is generally toward the river but also is influenced by the eastward ground surface elevation drop. There are, however, local areas where the flow direction differs due to differing hydraulic conductivities, land surface elevation and/or bedrock elevation changes, variations in recharge patterns, etc.

5.2.4 Estimating Up-Gradient Distance between Monitoring Wells and Selenium-Bearing Formations

The distance, L_s , between each monitoring well and the edge of an identified shale location was measured upstream along average ground water flow paths (i.e. perpendicular to water table contour lines in an up-gradient direction) using the ArcMAP™ (Version 9.2, ESRI 2006) measuring tool. The Arkansas River was assumed to be a ground water flow boundary. Since flow paths vary somewhat with time, the nearest shale deposit within +/- 15 degrees from the up-gradient direction from a well was used. A maximum distance from well to shale of 21 km was estimated using this method. Several wells in the Upstream Study Region and most wells in the Downstream Study Region did not have up-gradient identified shale deposits within this maximum distance. Well 12 in the Upstream Study Region is located on an identified shale deposit and therefore has $L_s = 0$ km. Tabular results of each well's L_s values are located in Appendix H.

5.2.5 Analysis of Constituent Concentrations in Relation to Up-Gradient Distance from Selenium-Bearing Formations

Pearson correlation coefficients, r_p , between L_s and other constituents in ground water in the Upstream region were computed using STATISTICA® (Version 9.0, StatSoft 2009). Correlations between C_{Se} and L_s , C_U and L_s , and C_{SO_4} and L_s , are presented in Table 5.5.

Table 5.5. Constituents Moderately and Strongly Correlated Constituents with L_s in Ground Water in the Upstream Region

Variable X	Variable Y	Correlation Relationship	r_p
C_{Se}	L_s	X-Log Y	-0.36
C_U	L_s	X-Log Y	-0.65
C_{SO_4}	L_s	X-Log Y	-0.69

These inverse correlations provide weight to the argument that underlying shale deposits are the primary source of these constituents in the LARV. Figures 5.72 through 5.74 illustrate these relationships as scatter plots of L_s vs. C_{Se} , L_s vs. C_U , and L_s vs. C_{SO_4} , respectively, in the Upstream Study Region.

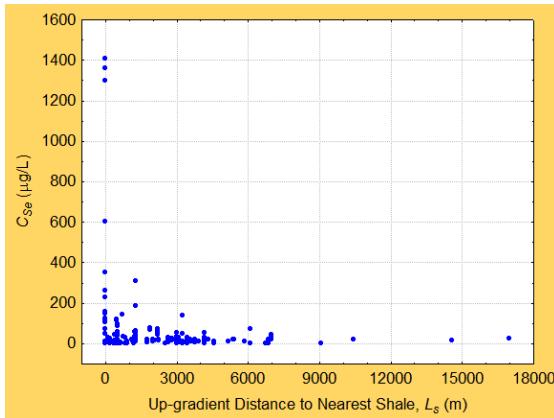


Figure 5.72. Scatter plot of C_{Se} vs. L_s in ground water samples from the Upstream Study Region

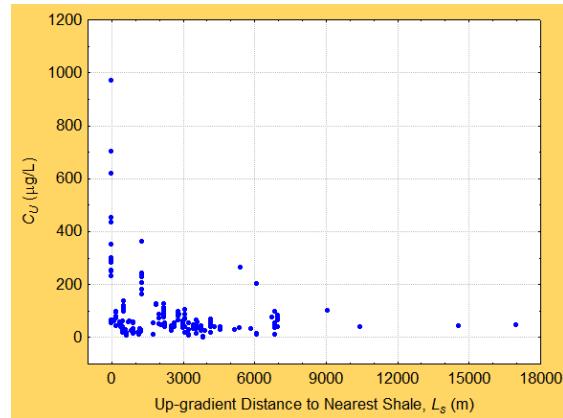


Figure 5.73. Scatter plot of C_U vs. L_s in ground water samples from the Upstream Study Region

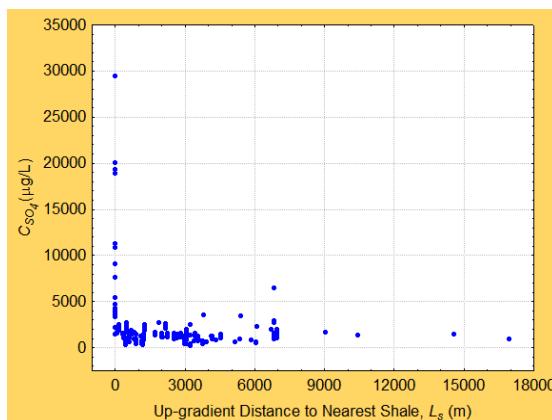


Figure 5.74. Scatter plot of C_{SO_4} vs. L_s in ground water samples from the Upstream Study Region

A possible multi-variate relationship between C_{Se} , C_{NO_3} , DO, and L_s was explored by first calculating the change in the r_p value between C_{Se} and L_s as a result of removing samples that contained little available oxygen. The marine shale deposits are expected to act as a dissolved Se source only if the ground water in contact contains DO or

NO_3^- . First, samples with levels of DO below a minimum threshold were removed. Several r_p values between C_{Se} and L_s were computed varying this DO threshold and the strongest correlation of $r_p = -0.60$ was found when excluding samples with $DO < 2.5 \text{ mg/L}$. Correlations between C_{Se} and L_s and C_{NO_3} also were explored by removing samples having low C_{NO_3} values.

The strongest correlation between C_{Se} and L_s ($r_p = -0.57$) was found when excluding samples with $C_{NO_3} < 24 \text{ mg/L}$ (approximately 75% of samples analyzed for C_{NO_3} did not meet this criteria).

Using both DO and C_{NO_3} thresholds, the strongest correlation between C_{Se} and L_s was $r_p = -0.77$, achieved by excluding samples containing $C_{NO_3} < 24 \text{ mg/L}$ and DO $< 2.5 \text{ mg/L}$ (approximately 50% of samples analyzed for both DO and C_{NO_3} did not meet this criteria).

Samples containing high C_{NO_3} or DO were then removed from the correlation data sets to see if high levels of selenium were found near shale locations in samples containing low values of C_{NO_3} or DO. When samples having $C_{NO_3} \geq 5 \text{ mg/L}$ were removed, the correlation between C_{Se} and L_s in the Upstream Study Region decreased to an insignificant, weak value of -0.16. This pattern also was evident with DO. When samples having DO $\geq 1.5 \text{ mg/L}$ were removed, the correlation between C_{Se} and L_s decreased to an insignificant, weak value of -0.18. These results suggest that marine shale deposits, thought to be a primary Se source in the LARV, do not contribute much to C_{Se} if either C_{NO_3} or DO is below certain “threshold” concentrations.

While C_{NO_3} and DO seem to play a key role in the oxidation of Se, several other factors such as pH, microbial activity, sediment oxygen-reduction potential, organic carbon content, and other constituent concentrations may greatly affect this process (Masscheleyn 1989, Neal et al. 1991, White et al. 1991, Jayaweera et al. 1996). Further research is essential to clearly defining how this process occurs in the LARV before strong conclusions may be made.

Chapter VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Over the past six years Colorado State University has conducted an extensive field study amassing a large data set of in-situ parameters and laboratory-tested constituent concentrations for the ground and surface waters of the LARV. The data gathered though this study and presented in this thesis provide substantial evidence of high Se concentrations in these waters. The average ground water C_{Se} is a factor of 3.2 and 1.7 times the current CDPHE livestock drinking water standard in the Upstream and Downstream Study Regions, respectively. The 85th percentiles values of C_{Se} in Arkansas River samples in both regions are approximately three or more times the current chronic standard of 4.6 µg/L for surface water. Maximum values of C_{Se} found in ground water samples were 1410 µg/L and 3760 µg/L while maximum values in the Arkansas River were 16.9 µg/L and 23.0 µg/L for the Upstream and Downstream Study Regions, respectively.

In addition to C_{Se} , three other constituent concentrations, C_B C_U , and $C_{Fe-Trec}$, exceeded CDPHE standards in the LARV. Maximum ground water C_B values of 428 mg/L in the Upstream Study Region and 162 mg/L in the Downstream Study Region greatly exceeded the CDPHE agricultural ground water acute standard of 0.75 mg/L. Maximum surface water C_U values of 197 µg/L in the Upstream Region and 138 µg/L in the Downstream Region greatly exceeded the MCL surface

water standard of 30 µg/L. The 85th percentile $C_{Fe-Trec}$ values greatly exceeded the aquatic life chronic surface water standard of 1.00 mg/L in the Arkansas River and tributaries of both regions. The Upstream and Downstream Study Regions were 12 and 2 times this standard, respectively.

It has been found that TDS are mostly composed of C_{SO_4} in both study regions. Average surface water TDS values increase markedly in the downstream direction along the river with the Upstream and Downstream Study Regions having values of 785 and 2904 mg/L, respectively. Measured EC also follows this trend with the Upstream and Downstream Study Regions having values of 1081 and 3281 dS/m, respectively.

C_{Se} in the LARV has been found to be strongly and significantly correlated with several other constituents, most predominantly C_U , C_{NO_3} , and C_{SO_4} . The relationships of C_{Se} vs. C_U and C_{SO_4} provide weight to the hypothesis that marine shale deposits are a primary source of these three constituents. High C_U or C_{SO_4} values may indicate the presence of an undiscovered underlying marine shale deposits. High correlations between C_{Se} and C_{NO_3} most likely result from NO₃ inducing Se mobilization from geological sources through redox reactions and preserving it in its most soluble form, selenate.

Contour plots and high spatial CV values reveal clear spatial patterns and substantial spatial variability over the studied LARV regions. CV values for all routine ground water C_{Se} were 266% and 140% for the Upstream and Downstream Study Regions, respectively. Spatial CVs for each sampling event ranged between 141% and 339% Upstream and between 105% and 188% Downstream.

Average ground water C_{Se} values per sampling event vary greatly over time. While the Upstream Study Region has only 8 sampling events, a linear least-squares best fit to sampling event routine ground water averages in the Downstream Study Region indicate that C_{Se} may have increased over the study period. Severe Se toxicity in the LARV may become a reality if this trend continues.

Fortunately, this research provides evidence that may be used to address this problem. Data analysis reveals that ground water in contact with marine shale deposits may require minimum concentrations of either DO or NO_3 to significantly mobilize and preserve dissolved Se. When samples having $C_{NO_3} \geq 5$ mg/L were removed from analysis the correlation between C_{Se} and L_s in the Upstream Study Region decreased to an insignificant, weak value of -0.16. This correlation increased greatly when only samples having sufficient NO_3 to mobilize Se were included. When samples having $C_{NO_3} \leq 12$ mg/L were removed, the correlation between C_{Se} and L_s increased to a significant, strong value of -0.51. This pattern also was evident with DO. When samples having DO ≥ 1.5 mg/L were removed the correlation between C_{Se} and L_s decreased to an insignificant, weak value of -0.18; however, when samples having DO ≤ 2 mg/L were removed, the correlation between C_{Se} and L_s increased to the significant, strong value of -0.57. The highest correlation between C_{Se} and L_s of -0.77 was achieved by only including samples containing $C_{NO_3} > 24$ mg/L and DO > 2.5 mg/L.

6.2 Recommendations

Previous research has shown that Se in selenium pyrite, $FeSe_2$, contained in marine shale deposits is oxidized into the soluble forms of SeO_3 and SeO_4 when these shales encounter water rich in DO or NO_3 . Results from the study reported herein support that this process is occurring

in the irrigated alluvial aquifer of Colorado's LARV. Naturally, reducing the amount of DO and NO_3 in contact with underlying marine shale deposits and their weathered residuum would retard the process of dissolving Se into ground water and consequently decrease Se loading to tributary streams and to the river.

Although it may be difficult to control concentrations of DO it is feasible to better manage NO_3 as well as the volume of water encountering shale and weathered shale deposits. Reducing oxygen enriched water in contact with shale deposits could be accomplished by regulating irrigation water and N fertilizer application, hence introducing less C_{NO_3} , especially on fields that are up-gradient to identified marine shale locations. Canal seepage losses also may be a significant source of ground water that comes in contact with underlying shale deposits. This may be mitigated by sealing or lining critical canal segments.

Discovery of other ways to improve Se source management, or the rate at which Se is released from sources such as shale and weathered shale deposits, begins with a more complete three-dimensional spatial and compositional identification of marine shale deposits in the LARV. This would identify additional Se sources and reduce model prediction uncertainty. Also, a better understanding of ground water flow paths taking into account irrigation and fertilization practices, hydraulic conductivities, and seasonal water table variations would give insight into choosing priority areas for implementing best management practices.

A calibrated ground water model would be very beneficial for use in evaluating the effectiveness of proposed mitigation strategies. Work is underway on developing such a model. A regional scale flow and mass transport model developed and applied to the LARV (Burkhalter and Gates

2005, 2006) is being refined and expanded to incorporate MODFLOW-2005 Unsaturated Zone Flow (UZF1), Recharge (RCH), and evapotranspiration (ET) packages. Other model updates include 1) replacement of uniform precipitation and potential ET with spatially-varying estimates, 2) more accurate estimations of ET using increased land and crop classification categories and remote sensing methods, 3) better temporal estimation of canal seepage losses, and 4) improved calibration using an expanded dataset (Morway 2010).

Additionally, work has begun to build and calibrate a local-scale 3-D Se transport model. Soil samples from the bedrock, mid-level alluvium, and topsoil have been taken to test for adsorbed Se concentrations as well as to provide a better understanding of NO_3 reduction and Se oxidation rates. A vertical transect has been established in the Upstream Study Region extending from the Arkansas River to near the edge of the unconfined aquifer close to the Rocky Ford Highline Canal. Samples taken from specified depths over time along this transect will hopefully form the basis of this new model and provide a more complete picture of how Se is transported in the LARV. The long term goal of this project is to test proposed solutions against a fully-calibrated regional scale Se transport model. (Bailey 2010).

Over-application of NO_3 fertilizers and irrigation water, as well as excessive canal seepage, above and up-gradient of underlying marine shale deposits seems a key factor in Se mobilization, and thereby in increasing Se concentrations in the LARV. By designing best management practices guided by the findings presented in this thesis, water resource managers in the LARV might be able to substantially lower the concentrations of dissolved Se in the ground and surface water thereby reducing the likelihood of Se toxicity. However, due to the complex nature of the problem of Se mobilization, continued research is essential to identifying

and implementing these best management practices. There are several minor improvements to the sampling plan that may increase the efficiency and effectiveness of our research.

The current dataset appears to be quite complete; however, it would be beneficial to gather Manganese (Mn) samples. This is because Mn lies just before selenate on the redox ladder and may be correlated with C_{Se} . Also, it would be beneficial to sample for selenite in the surface water of the Upstream Study Region to validate our assumption that approximately 90% of C_{Se} is in the form of selenate. The dataset may be further improved by sampling more wells located within or very near (down-gradient) known shale deposits. It would be interesting to see if these wells also consistently yield high values of C_{Se} , C_U , and C_{SO_4} .

The quality of gathered data may be improved by refining the calibration of the *YSI 600QS Multiparameter Sampling System™*. Keeping more rigorous equipment calibration and maintenance records would identify equipment that is prone to failure, reduce the chance of over-maintaining (i.e. accidentally calibrating for ORP every two months while it actually is required every six months), and increase measurement accuracy. Also, it recently has been discovered that there may be more efficient calibration and storage methods, which may extend equipment life. Meeting with our equipment supplier for training will be an excellent way to thoroughly understand any improved methods available.

An improvement in personnel training also would prove beneficial to not only dataset quality but also the efficiency with which data are collected. More detailed sampling procedures are needed. Also, increasing the overlap between successive personnel in charge of sampling

provides more time spent learning from an experienced sampler in the field. This is very valuable when problems or abnormalities arise.

REFERENCES

Afzul, S., Younas, M., Ali, K. (2000) "Selenium speciation studies from Soan-Sakesar Valley, Salt Range, Pakistan." *Water International*. 25(3), 425-436.

Alfthan, G., Wang, D., Aro, A., and Soveri, J. (1995) "The geochemistry of selenium in groundwaters in Finland" *Science of the Total Environment*. 162(2-3), 93-103.

Bailey, R. PhD Candidate, Dept. Civil and Environmental Engineering, Colorado State University, Fort Collins (personal communication, 2010).

Banuelos, G.S., Lin, Z.Q., Arroyo, I., and Terry, N. (2005) "Selenium volatilization in vegetated agricultural drainage sediment from the San Luis Drain, Central California." *Chemosphere*. 60, 1203-1213.

Beisner, K., Naftz, D., Johnson, W., and Diaz, X. (2009) "Selenium and trace element mobility affected by periodic displacement of stratification in the Great Salt Lake, Utah." *Science of the Total Environment*. 407, 5263-5273.

Burkhalter, J.P., and Gates, T.K. (2005). "Agroecological impacts from salinization and waterlogging in an irrigated river valley." *Journal of Irrigation and Drainage Engineering*, 131(2), 197-209.

Burkhalter, J.P., and Gates, T.K. (2006). "Evaluating regional solutions to salinization and waterlogging in an irrigated river valley." *Journal of Irrigation and Drainage Engineering*, 132(1), 21-30.

Byers, H.G., Williams, K.T., and Lakin, H.W. (1936). "Selenium in Hawaii and its probable source in the United States." *Industrial and Engineering Chemistry*, 28(7), 821-823.

Cain, D. (1985). "Quality of the Arkansas River and Irrigation-Return Flows in the Lower Arkansas River Valley, Colorado." WRI 84-4273, United States Geological Survey, Lakewood, CO.

USDA Census of Agriculture. Retrieved 2010 from the United States Department of Agriculture. Website: www.agcensus.usda.gov.

Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission (WQCC) (2009a). "Regulation number 31 – The basic standards and methodologies for surface water", 56. Retrieved 2010 Website: www.cdphe.state.co.us

Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission (WQCC) (2009b). "Regulation number 41 – The basic standards for ground water, 21." Retrieved 2010 Website: www.cdphe.state.co.us

Colorado Department of Public Health and Environment (CDPHE), Colorado Water Quality Control Commission (2002a). "Status of water quality in Colorado." Retrieved 2010 Website: www.cdphe.state.co.us

Colorado Department of Public Health and Environment (CDPHE), Colorado Water Quality Control Commission (2002b). "Pre-hearing statement for revision of regulation No. 32, exhibit 2: rationale." Retrieved 2010 Website: www.cdphe.state.co.us

Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission (WQCC) (2002c). "Water quality limited segments still requiring TMDLs – Colorado's 2002 section 303(d) list and monitoring and evaluation list, 46." Retrieved 2010 Website: www.cdphe.state.co.us

Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission (WQCC) (2003). "Regulation number 32 – Classification and numerical standards for Arkansas River Basin, 81." Retrieved 2010 Website: www.cdphe.state.co.us

Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission (WQCC) (2004a). "Regulation number 93 2004 section 303(d) list water-quality-limited segments requiring TMDLs." Retrieved 2010 Website: www.cdphe.state.co.us

Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission (WQCC) (2004b). "Regulation number 94 Colorado's monitoring and evaluation list." Retrieved 2010 Website: www.cdphe.state.co.us

Cota, T.F., Chott, T.M., and Waesche, K.L. (2005) "RCRA Facility Investigation; Solid Waste Management Unit No. 82; Selenium in Groundwater" Environmental Resource Management Report, Pueblo, CO.

Debruyn, A., and Chapman, P. (2007) "Selenium toxicity to invertebrates: Will proposed thresholds for toxicity to fish and birds also protect their prey?" *Environmental Science & Technology*. 41, 1766-1770.

Deverel, S.J. and Fujii, R. (1988) "Processes affecting the distribution of selenium in shallow groundwater of agricultural areas, western San Joaquin valley, California." *Water Resources Research*. 24(4), 516-524.

Deverel, S.J. and Gallanthine, S.K. (1989). "Relation of salinity and selenium in shallow groundwater to hydrologic and geochemical processes, western San Joaquin Valley, California." *Journal of Hydrology*, 109(1-2), 125-149.

Deverel, S.J. and Millard, S.P. (1988). "Distribution and mobility of selenium and other trace elements in shallow groundwater of the western San Joaquin Valley, California." *Environmental Science & Technology*, 22(6), 697-702.

Elarashidi, M.A., Adriano, D.C., Workman, S.M. and Lindsay, W.L. (1987) "Chemical Equilibria of Selenium in Soils: A Theoretical Development." *Soil Science*, 144(2), 141-152.

Engberg, R.A. and Sylvester, R.A. (1993) "Concentrations, distributions, and sources of selenium from irrigated lands in western United States." *Journal of Irrigation and Drainage Engineering*. 119(3), 522-536.

Environmental Protection Agency. Retrieved 2010. Website: www.epa.gov

Evans, M., Hastings, N., and Peacock, B. (1993). *Statistical Distributions*, John Wiley & Sons, Inc. New York, NY.

Fio, J.L., Fujii, R., and Deverel, S.J. (1991). "Selenium mobility and distribution in irrigated and nonirrigated alluvial soils." *Soil Science Society of America Journal*, 55(5), 1313-1320.

Fujii, R. and Deverel, S.J. (1989). "Mobility and distribution of selenium and salinity in ground-water and soil of drained agricultural fields, western San Joaquin Valley of California." *Selenium in Agriculture and the Environment*, New Orleans, LA, Soil Science Society of America, Inc., 233.

Gates, T.K., Cody, B.M., Donnelly, J.P., Herting, A.W., Bailey, R.T., and Mueller-Price, J. (2009) "Assessing selenium contamination in the irrigated stream-aquifer system of the Arkansas River, Colorado" *Journal of Environmental Quality*. 38, 2344-2356.

Gates, T.K., Garcia, L.A., Labadie, J.W. (2006). "Toward optimal water management in Colorado's Lower Arkansas River Valley: Monitoring and modeling to enhance agriculture and environment" Completion Report No. 205 to the Colorado Water Resources Research Institute, Colorado State University, Department of Civil and Environmental Engineering, Fort Collins, CO.

Gates, T.K., Burkhalter, J.P., Labadie, J.W., Valliant, J.C., and Broner, I. (2002). "Monitoring and modeling flow and transport in a salinity-threatened irrigated valley." *Journal of Irrigation and Drainage Engineering*, 128(2), 87-99.

Gauch, R. (2000). *Statistical Methods for Researchers Made Very Simple*, University Press of America, Inc. Lanham, MD.

Geering, H.R. Cary, E.E., Jones, L.H.P., and Allaway, W.H. (1968). "Solubility and redox criteria for the possible forms of selenium in soil." *Soil Science Society of America Proceedings*, 32, 35-40.

Ghassemi, F., Jakeman, A.J., and Nix, H.A. (1995). *Salinization of Land and Water Resources: Human causes, extent, management and case studies*, University of New South Wales Press LTD, Sydney, Australia.

Gilbert, R.O. (1987). *Statistical methods for Environmental Pollution Monitoring*, John Wiley & Sons, Inc. New York, NY.

Goss, M.J., Barry, D.A.J., and Rudolph, D.L. (1998) "Contamination in Ontario farmstead domestic wells and its association with agriculture: 1. Results from drinking water wells." *Journal of Contaminant Hydrology*. 32, 267-293.

Ham, Y. and Tamiya, S. (2006) "Selenium behavior in open bulk precipitation, soil solution and groundwater in alluvial fan area in Tsukui, Central Japan." *Water, Air, and Soil Pollution*. 177(1-4), 45-57.

Hamilton, S.J. (2002). "Rationale for a tissue-based selenium criterion for aquatic life." *Aquatic Toxicology*, 57(1-2), 85-100.

Hamilton, S.J. and Lemly A.D. (1999). "Water-sediment controversy in setting environmental standards for selenium." *Ecotoxicology and Environmental Safety*, 44(3), 227-235.

Hine, S.E., Gardner, E., and Hoag, D. (2000). *Colorado's Agribusiness System: Its Contribution to the State Economy*, Final Report to the Colorado Department of Agriculture, Colorado State University, Department of Agricultural and Resource Economics, Fort Collins, CO.

Hu, X., Wang, F., and Hanson, M.L. (2009) "Selenium concentration, speciation and behavior in surface waters of the Canadian prairies." *Science of the Total Environment*. 407, 5869-5876.

Hudak, P.F. (2004) "Boron and selenium contamination in south Texas groundwater." *Journal of Environmental Science and Health*. A39(11-12), 2827-2834.

Hunter, W. (2006) "Removing selenate from groundwater with a vegetable oil-based biobarrier." *Current Microbiology*. 53, 244-248.

Jawaweera G.R. and Biggar J.W. (1996). "Role of redox potential in chemical transformations of selenium in soils." *Soil Science Society of America Journal*, 60(4), 1056-1063.

Karlson, U. and Frankenberger, W.T. (1989) "Accelerated rates of selenium volatilization from California soils." *Soil Science Society American Journal*. 53, 749-753.

Komroff, Ed., Jr. (1926). *The Travels of Marco Polo (The Venetian)*, (Revised from Marsdens' translation and edited with an introduction). New York, NY.

Korom, S.F. (1992) "Natural denitrification in the saturated zone, A review". *Water Resources Research*. 28(6), 1657-1668.

Lakin, H.W. and Byers, H.G. (1941). *Selenium Occurrence in Certain Soils in the United States, With a Discussion of Related Topics: Sixth Report*, Technical Bulletin No. 783, United States department of Agriculture, Washington, D.C.

Lemly, A.D. (2004). "Aquatic selenium pollution is a global environmental safety issue." *Ecotoxicology and Environmental Safety*, 59(1), 44-56.

Lemly, A.D. (2002a) "Symptoms and implications of selenium toxicity in fish: the Belews Lake case example." *Aquatic Toxicology*. 57, 39-49.

Lemly, A.D. (2002b) "A procedure for setting environmentally safe total maximum daily loads (TMDLs) for selenium." *Ecotoxicology and Environmental Safety*. 52, 123-127.

Lenz, M. and Lens, P.N.L. (2009) "The essential toxin: The changing perception of selenium in environmental sciences." *Science of the Total Environment*. 407, 3620-3633.

Li, Y., Wang, W., Luo, K., and Li, H. (2008) "Environmental behaviors of selenium in soil of typical selenosis area, China." *Journal of Environmental Sciences*. 20, 859-864.

Lindburg, R.D. and Runnels, D.D. (1984). "Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling." *Science*, 225(4665), 925-927.

Martens, D.A. and Suarez, D.L. (1997). "Selenium speciation of marine shales, alluvial soils, and evaporation basin soils of California." *Journal of Environmental Quality*, 26(2), 424-432.

Masscheleyn, P.H., Delaune, R.D., and Patrick, W.H. (1990) "Transformations of selenium as affected by sediment oxidation-reduction potential and pH." *Environmental Science & Technology*. 24, 91-96.

May, W. et al. (2008) "An evaluation of selenium concentrations in water, sediment, invertebrates, and fish from the Solomon River Basin." *Environmental Monitoring and Assessment*. 137, 213-232.

McGregor, A.L. et al. (2008) "Plant uptake and leaching of selenium in manure and gypsum-amended soils of the Western Phosphate Resource Area." *Soil Science*. 173(9), 613-623.

McNeal, J.M. and Balistrieri, L.S. (1989). "Geochemistry and occurrence of selenium: An overview." *Selenium in Agriculture and the Environment*, Soil Science Society of America, Inc., New Orleans, LA, 233.

Morway, E. PhD Candidate, Dept. Civil and Environmental Engineering, Colorado State University, Fort Collins (personal communication, 2010).

Mueller, D.K., DeWeese, L.R., Garner, A. J., and Spruill, T.B. (1992). "Reconnaissance investigation of water quality, bottom sediment, and biota associated with irrigation drainage in the Middle Arkansas River Basin, Colorado and Kansas, 1988-89." WRI 91-4060, United States Geological Survey, Denver, CO.

Mueller-Price, J.M. and Gates, T.K. (2008) "Assessing uncertainty in mass balance calculation of river nonpoint source loads." *Journal of Environmental Engineering*. 134(4), 247-258.

Muscatello, J.R., Belknap, A.M., Janz, D.M. (2008) "Accumulation of selenium in aquatic systems downstream of a uranium mining operation in northern Saskatchewan, Canada." *Environmental Pollution*. 156, 387-393.

Nace, R.L. (1972). "Water problems and developments of the past." *Water Resources Bulletin*, 8(1), 101-109.

National Academy of Science, The National Research Council, Committee on Medical and Biological Effects of Environmental Pollutants, Division of Medical Sciences (NAS-NRC) (1976). *Selenium*, National Academy Press, Washington, D.C.

National Academy of Science, The National Research Council, Committee on Irrigation-Induced Water Quality Problems (NAS-NRC) (1989). *Irrigation-Induced Water Quality Problems What Can Be Learned from the San Joaquin Valley Experience*, National Academy Press, Washington, D.C.

National Irrigation Water Quality Program (NIWQP). Retrieved 2010 from the United States Bureau of Reclamation. Website: www.usbr.gov/niwqp.

Neal, R.H and Sposito, G. (1991) "Selenium mobility in irrigated soil columns as affected by organic carbon amendment." *Journal of Environmental Quality*. 20, 808-814.

Neal, R.H., Sposito, G., Holtzclaw, K.M., and Traina, S.J. (1987a). "Selenite adsorption on alluvial soils: I. Soil composition and pH effects." *Soil Science Society of America Journal*, 51(5), 1161-1165.

Neal, R.H., Sposito, G., Holtzclaw, K.M., and Traina, S.J. (1987b). "Selenite adsorption on alluvial soils: II. Solution composition effects." *Soil Science Society of America Journal*, 51(5), 1165-1169.

Nelson, B.N. et al. (2003) "In situ, anaerobic, biological immobilization of uranium, molybdenum and selenium in an alluvial aquifer." *Mining Engineering*. 55(3), 31-36.

Nolan, B.T., Ruddy, B.C., Hitt, K.J., and Helsel, D.R. (1997) "Risk of nitrate in groundwaters of the United States – A national perspective." *Environmental Science and Technology*. 31, 2229-2236.

Ohlendorf, H.M., Hothem, R.L., Bunck, C.M., and Marois, K.C. (1990) "Bioaccumulation of selenium in birds at Kesterson Reservoir, California" *Environmental Contamination & Toxicology*. 19, 495-507.

Ortiz, R.F., Lewis, M.E., and Radell, M.J. (1998). "Water-quality assessment of the Arkansas River basin, Southeastern Colorado, 1990-93" WRI 97-4111, United States Geological Survey, Denver, CO.

Presser, T.S., Sylvester, M.A., and Low W.H. (1994) "Bioaccumulation of selenium from natural geologic sources in western states and its potential consequences." *Environmental Management*. 18(3), 423-436.

Presser, T.S. (1994). "The Kesterson Effect." *Environmental Management*, 18(3), 437-454.

Presser, T.S. and Swain, W.C. (1990) "Geochemical evidence for Se mobilization by the weathering of pyritic shale, San Joaquin Valley, California, U.S.A." *Applied Geochemistry*. 5, 703-717.

Puls, R.W. and Barcelona, M.J. (1996). *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*, EPA/540/S-95/504. US Environmental Protection Agency, Washington, D.C.

Riley, J.P. and Jurinak, J.J. (1979). "Irrigation management for river-salinity control." *Journal of Irrigation and Drainage Engineering*, 105(4), 419-432.

Roenfeld, I. and Beath, O.A. (1964). "Chemistry of selenium." In I. Rosenfeld, *Selenium. Geobotany, Biochemistry, Toxicity, and Nutrition*, New York: Academic Press pp. 299-332.

Rosenk B.P. and Zijuan, L. (2009) "Transport pathways for arsenic and selenium: A minireview." *Environmental International*. 35, 512-515.

Runnels D.D. and Lindburg, R.D. (1990). "Selenium in aqueous-solutions – Impossibility of obtaining a meaningful EH using a platinum-electrode, with implications for modeling of natural-waters." *Geology*, 18(3), 212-215.

Sager, M. (2006) "Selenium in agriculture, food, and nutrition" *Pure Applied Chemistry*. 78(1) 111-133.

Sarathchandra, S.U., and Watkinson, J.H. (1981). "Oxidation of elemental selenium to selenite by bacillus megaterium." *Science*, 211(4482), 600-601.

Sarquis, M. and Mickey, C.D. (1980). "Selenium part 1: Its chemistry and occurrence." *Journal of Chemical Education*, 57(12), 886-889.

Scanlon, B.R., Jolly, I., Sophocleous, M., and Zhang, L. (2007) "Global impacts of conversions from natural to agricultural ecosystems on water resources: Quantity versus quality." *Water Resources Research*. 43, 1029-1046.

Scott, G.R. (1968). "Geologic and structure contour map of the La Junta quadrangle, Colorado and Kansas", United States Geological Survey, Washington, D.C.

Scott, G.R. et al. (1978). "Geologic map of the $1^{\circ} \times 2^{\circ}$ quadrangle, south-central Colorado", United States Geological Survey, Reston, VA.

Schuler, C.A., Anthony, R.G., and Ohlendorf, H.M. (1990) "Selenium in wetlands and waterfowl foods at Kesterson Reservoir, California, 1984." *Environmental Contamination and Toxicology*. 19, 845-853.

Seiler, R.L., Skorupa, J.P., and Peltz, L.A. (1999). "Areas susceptible to irrigation-induced selenium contamination of water and biota in the Western United States." Circular 1180, United States Geological Survey, Denver, CO.

Sharps, J.A. (1976). "Geological map of the Lamar Quadrangle, Colorado and Kansas." United States Geological Survey, Reston, VA.

Sherow, J.E. (1990). *Watering the Valley*. University Press of Kansas. Lawrence, KS.

Sposito, G., Yang, A., Neal R.H., and Mackzum, A. (1991). "Selenate reduction in an alluvial soil." *Soil Science Society of America Journal*, 55(6), 1597-1602.

StatSoft, Inc. (2010). STATISTICA (data analysis software) version 9.1, Tulsa, OK.

Storet Data. Retrieved 2010 from the Environmental Protection Agency. Website: www.epa.gov/storet

Tidball, R.R., Severson, R.C., Presser, T.S., and Swain W.C. (1991). "Selenium sources in the Diablo Range, Western Fresno County, California." In Severson, R.C., Fisher, S.E., Jr., and Gough, L.P., eds. (1991). Proceeding of the 1990 Billings land Reclamation Symposium of Selenium in Arid and Semiarid Environments, Western United States, Circular 1064, United States Geological Survey, Denver, CO. pp. 107-114.

Tracy, J.E., Oster J.D., and Beaver R.J. (1990) "Selenium in the southern coast range of California: Well waters, mapped geological units, and related elements." *Journal of Environmental Quality*. 19, 46-50.

Trelease, S.F. and Beath, O.A. (1949). *Selenium – Its Geological Occurrence and Its Biological Effects in Relation to Botany, Chemistry, Agriculture, Nutrition, and Medicine*. New York, NY.

Triana, E., Labadie, J.W., and Gates, T.K. (2010a) "River GeoDSS for agroenvironmental enhancement of Colorado's Lower Arkansas River Basin. I: Model development and calibration." *Journal of Water Resources Planning and Management*, 136(2), 177-189.

Triana, E., Labadie, J.W., and Gates, T.K. (2010b) "River GeoDSS for agroenvironmental enhancement of Colorado's Lower Arkansas River Basin. II: Evaluation of strategies." *Journal of Water Resources Planning and Management*, 136(2), 190-200.

Triana, E., Labadie, J.W., and Gates, T.K. (2007). "Regional-to-basin scale evaluation of water management strategies along a salinity-affected river valley." Proceedings of the international Salinity Forum, ASCE, Riverside, CA.

Umysova, D. et al. (2009) "Bioaccumulation and toxicity of selenium compounds in the green alga *Scenedesmus quadricauda*." *BMC Plant Biology*. 9, 58-73.

U.S. Environmental Protection Agency, Office of Water (1996). "Method 1669 sampling ambient water for trace metals at EPA water quality criteria levels". US Environmental Protection Agency, Washington D.C.

U.S. Environmental Protection Agency, Office of Water (1999). "National recommended water quality criteria – correction". Report No. EPA 822-Z-99-001, US Environmental Protection Agency, Washington D.C.

U.S. Environmental Protection Agency, Office of Water (2002). "National water quality inventory 2000 report". Report No. EPA-841-R-02-01, US Environmental Protection Agency, Washington D.C.

USGS Water Data for the Nation. Retrieved 2010 from the United States Geological Survey.
Website: www.waterdata.usgs.gov

United States Geological Survey. Retrieved 2010 Website: www.usgs.gov

Voegeli, P.T. and Hershey, L.A. (1965). "Geology and ground-water resources of Prowers County, Colorado." Geological Survey Water-Supply Paper 1772, United States Department of the Interior, Washington, D.C.

Voegeli, P.T. (1963). "Ground water in Colorado – Its importance during an emergency" Ground-Water Series Circular 9, Colorado Water Conservation Board, Denver, CO.

Watts, K. Pueblo Subdistrict Office, U.S. Geological Survey (personal communication, 2008)

Weres, O. et al. (1990) "The effect of nitrate and organic matter upon mobility of selenium in groundwater and in a water treatment process." *Water, Air, and Soil Pollution*. 49, 251-272.

White, A.F., Benson, S.M., Yee, A.W., Wollenberg, H.A., and Flexser, S. (1991). "Groundwater contamination at Kesterson Reservoir, California 2. Geochemical parameters influencing selenium mobility." *Water Resource Research*, 27(6), 1085-1098.

Whittemore, D.O. (2009) "Selenium loss in the Arkansas River across the High Plains, USA." *Geological Society of America: Abstracts with Programs*, 41(7), 201.

Wright, W.G. (1999). "Oxidation and mobilization of selenium by nitrate in irrigation drainage." *Journal of Environmental Quality*, 28(4), 1182-1187.

Wu, L. (2004) "Review of 15 years of research on ecotoxicology and remediation of land contaminated by agricultural drainage sediment rich in selenium." *Ecotoxicology and Environmental Safety*. 57, 257-269.

Yamada, H., Kamada, A., Usuki, M., and Yanai, J. (2009) "Total selenium content of agricultural soils in Japan." *Soil Science and Plant Nutrition*. 55, 616-622.

YSI. Retrieved 2010 Website: www.y si.com

Zhu, J. et al. (2008) "Distribution and transport of selenium in Yutangba, China: Impact of human activities." *Science of the Total Environment*. 392, 252-261.

Zielinski, R.A., Asher-Bolinder, S., and Meier, A.L. (1995). "Uraniferous waters of the Arkansas River Valley, Colorado, USA: A function of geology and land use." *Applied Geochemistry*, 10(2), 133-144.

Zieve, R. and Peterson, P.J. (1981) "Factors Influencing the volatilization of selenium from soil." *The Science of the Total Environment*. 19, 277-284.

Zieve, R. and Peterson, P.J. (1984) "Volatilization of selenium from plants and soils." *The Science of the Total Environment*. 32, 197-202.

APPENDIX A – Sample Surface Water Sampling Form

Colorado State University
 Department of Civil
 Engineering
 Arkansas River Assessment

Surface Water Sampling Log

Surface Water Station No.:	Sample Location (w/ respect to river, canal, or drain)
Station Location:	Comments:
Date/Time:	
Sample collector(s):	
Sample location	

Time (min)	pH	Temp (°C)	Sp. Cond. ($\mu\text{g}/\text{cm}$)	Dis. O ₂ (mg/L)	ORP (mV)	Notes

APPENDIX B – Sample Ground Water Sampling Form

Colorado State University
Department of Civil Engineering
Arkansas River Assessment

Well Sampling Log

Well No.:	Height of Water Column: (Well Depth - Depth to Water)
Date:	Depth of pump intake:
Sample collector(s):	(Water level + 1/2 Water Column)
Depth to Water*:	Comments:
Well Depth*:	Pump Start Time:
Height of Casing:	ID:

*From top of casing

**Units in feet

Colorado State University
Department of Civil Engineering
1372 Campus Delivery
Fort Collins, CO 80526-1372

APPENDIX C – Sample Chain of Custody Form

CHAIN OF CUSTODY RECORD
Arkansas River Assessment

APPENDIX D – Histograms of Fe-Trec and SO₄

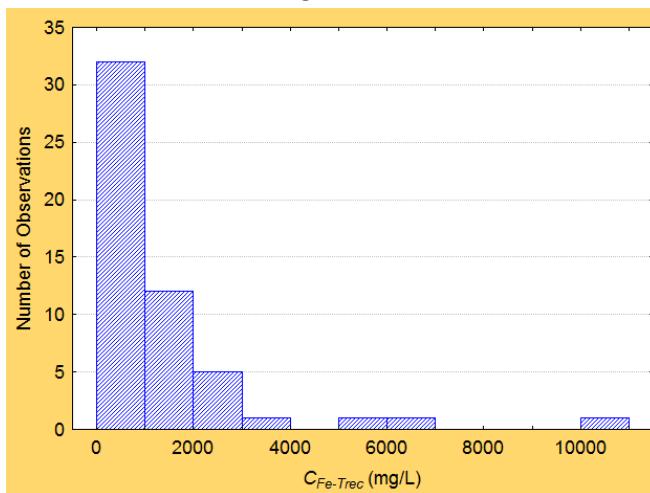


Figure D.1. Histogram of $C_{Fe-Trec}$ from routine samples gathered from ground water in the Downstream Study Region

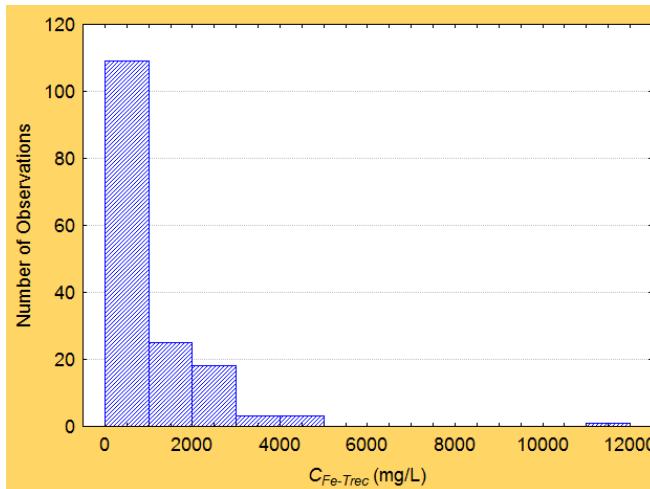


Figure D.2. Histogram of $C_{Fe-Trec}$ from routine samples gathered from the Arkansas River in the Downstream Study Region

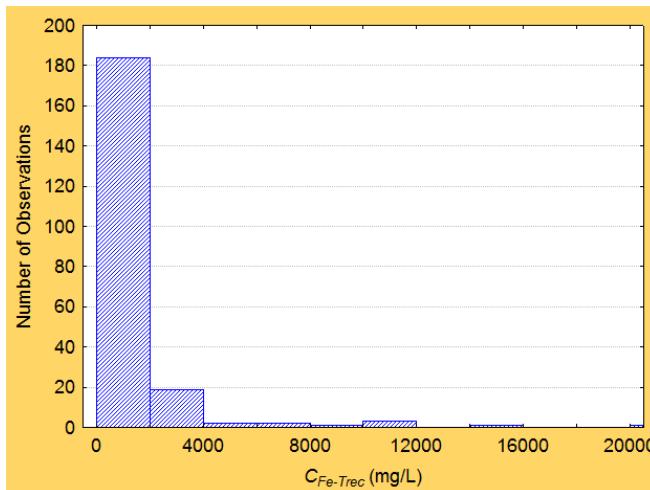


Figure D.3. Histogram of $C_{Fe-Trec}$ from routine samples gathered from tributaries and drains in the Downstream Study Region

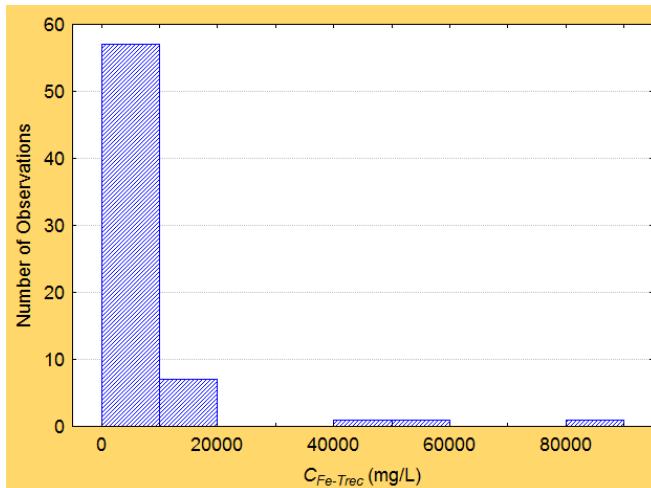


Figure D.4. Histogram of $C_{Fe-Trec}$ from routine samples gathered from canals in the Downstream Study Region

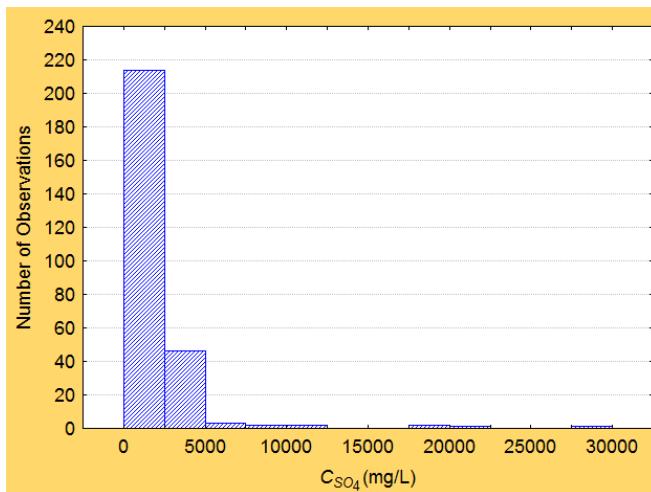


Figure D.5. Histogram of C_{SO_4} from routine samples gathered from ground water in the Upstream Study Region

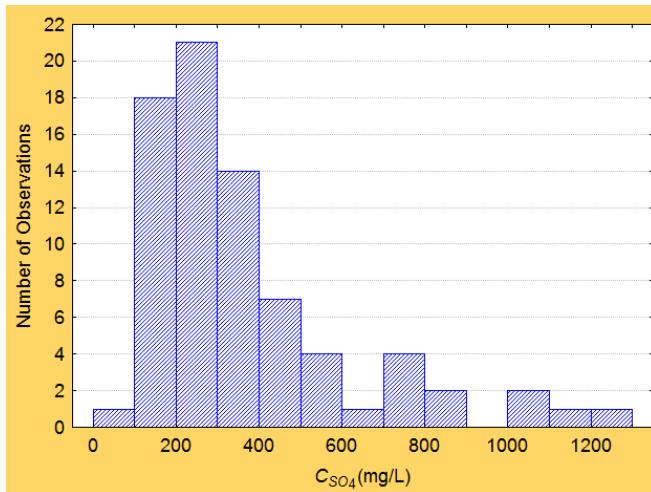


Figure D.6. Histogram of C_{SO_4} from routine samples gathered from the Arkansas River in the Upstream Study Region

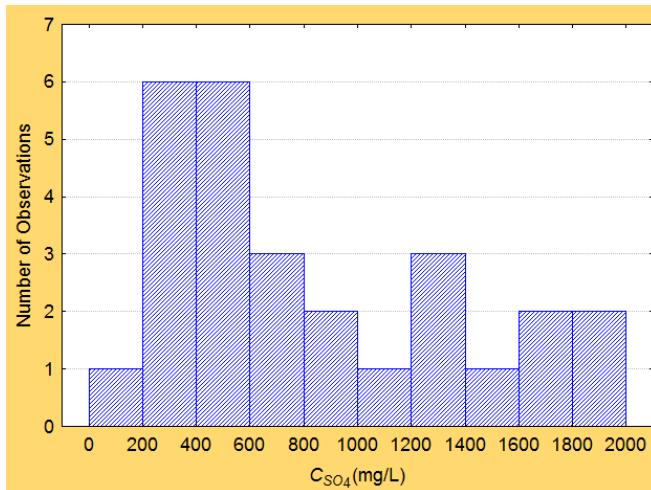


Figure D.7. Histogram of C_{SO_4} from routine samples gathered from tributaries and drains in the Upstream Study Region

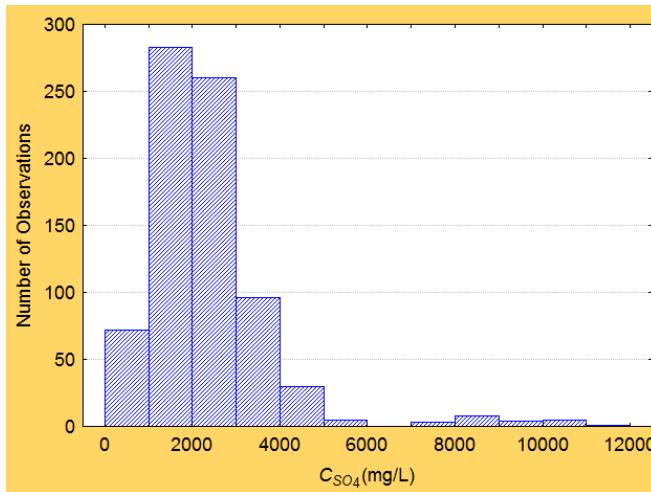


Figure D.8. Histogram of C_{SO_4} from routine samples gathered from ground water in the Downstream Study Region

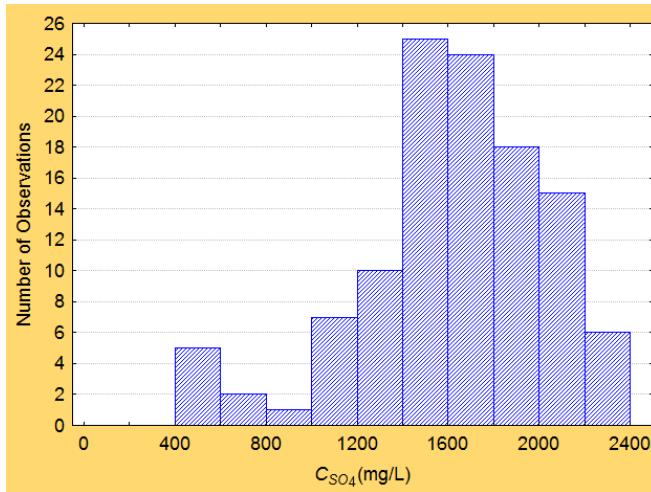


Figure D.9. Histogram of C_{SO_4} from routine samples gathered from the Arkansas River in the Downstream Study Region

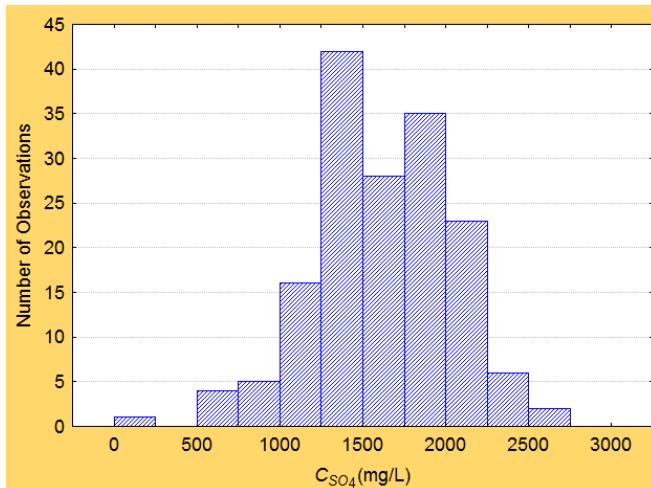


Figure D.10. Histogram of C_{SO_4} from routine samples gathered from tributaries and drains in the Downstream Study Region

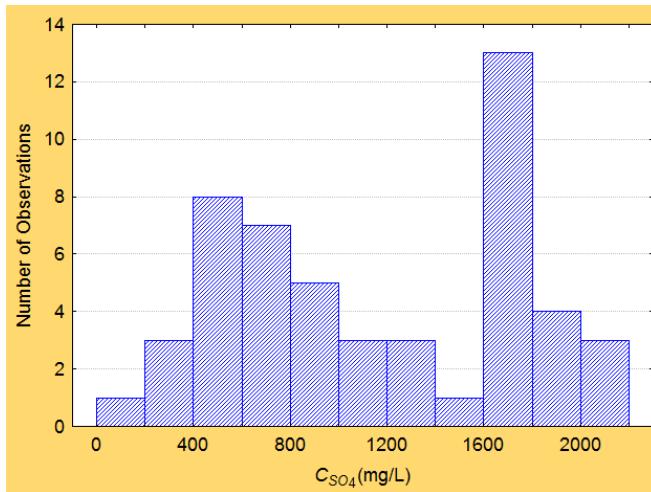


Figure D.11. Histogram of C_{SO_4} from routine samples gathered from canals in the Downstream Study Region

APPENDIX E— r_p Values between All Constituents in the Upstream Ground Water

	Ls	Log Ls	WT Depth	Log WT Depth	Field pH	Log Field pH	T	Log T	Field EC	Log Field EC	DO	Log DO	ORP	Log ORP
Ls	1.00	0.68	-0.06	-0.02	0.09	0.09	0.05	0.07	-0.19	-0.11	0.06	-0.03	0.18	0.10
Log Ls	0.68	1.00	0.03	0.08	0.14	0.14	0.05	0.08	-0.63	-0.32	0.07	0.00	0.05	-0.03
WT Depth	-0.06	0.03	1.00	0.93	0.05	0.05	-0.03	0.02	-0.17	-0.12	0.39	0.34	0.17	0.05
Log WT Depth	-0.02	0.08	0.93	1.00	0.05	0.05	-0.03	0.01	-0.14	-0.05	0.35	0.32	0.16	0.03
Field pH	0.09	0.14	0.05	0.05	1.00	1.00	-0.09	-0.12	-0.12	-0.11	0.15	0.10	-0.16	-0.15
Log Field pH	0.09	0.14	0.05	0.05	1.00	1.00	-0.09	-0.12	-0.12	-0.11	0.15	0.10	-0.16	-0.14
T	0.05	0.05	-0.03	-0.03	-0.09	-0.09	1.00	0.89	-0.02	0.00	-0.06	-0.05	-0.04	-0.14
Log T	0.07	0.08	0.02	0.01	-0.12	-0.12	0.89	1.00	-0.06	-0.06	-0.04	-0.04	-0.07	-0.15
Field EC	-0.19	-0.63	-0.17	-0.14	-0.12	-0.12	-0.02	-0.05	1.00	0.67	-0.08	-0.04	-0.01	0.04
Log Field EC	-0.11	-0.32	-0.12	-0.05	-0.11	-0.11	0.00	-0.06	0.67	1.00	-0.10	-0.07	-0.01	0.06
DO	0.06	0.07	0.39	0.35	0.15	0.15	-0.06	-0.04	-0.08	-0.10	1.00	0.88	0.24	0.18
Log DO	-0.03	0.00	0.34	0.32	0.10	0.10	-0.05	-0.04	-0.04	-0.07	0.88	1.00	0.25	0.16
ORP	0.18	0.05	0.17	0.16	-0.16	-0.16	-0.04	-0.07	-0.07	-0.01	0.24	0.25	1.00	0.87
Log ORP	0.10	-0.03	0.05	0.03	-0.15	-0.14	-0.14	-0.15	0.04	0.06	0.18	0.16	0.87	1.00
Se	-0.19	-0.36	-0.08	-0.05	-0.10	-0.10	-0.01	-0.02	0.38	0.31	0.01	0.05	-0.04	0.07
Log Se	-0.09	-0.12	-0.05	-0.02	-0.08	-0.07	0.01	-0.02	0.32	0.35	0.20	0.28	0.16	0.10
Fe	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
Log Fe	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
U	-0.24	-0.65	-0.19	-0.18	-0.11	-0.10	-0.02	-0.07	0.68	0.44	-0.08	-0.01	-0.03	0.01
Log U	-0.15	-0.39	-0.25	-0.21	-0.13	-0.12	0.00	-0.06	0.58	0.57	-0.10	-0.01	0.00	0.01
Fe-Trec	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
Log Fe-Trec	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
Lab pH	0.15	0.16	0.07	0.06	0.77	0.77	-0.05	-0.01	-0.11	-0.15	0.13	0.08	-0.23	-0.26
Log Lab pH	0.14	0.15	0.07	0.05	0.77	0.77	-0.04	-0.01	-0.11	-0.14	0.13	0.08	-0.23	-0.26
SAR	-0.18	-0.70	-0.22	-0.21	-0.19	-0.19	0.00	-0.04	0.81	0.50	-0.12	-0.08	-0.01	0.03
Log SAR	-0.12	-0.50	-0.32	-0.28	-0.22	-0.22	0.02	-0.04	0.67	0.55	-0.20	-0.16	-0.03	0.02
Adj SAR	-0.01	-0.02	-0.16	-0.12	-0.18	-0.19	0.04	0.03	0.24	0.34	-0.11	-0.10	0.01	0.01
Log Adj SAR	0.12	0.45	-0.08	-0.04	-0.08	-0.08	0.04	0.04	-0.24	0.08	-0.10	-0.12	0.01	-0.03
Lab EC	-0.19	-0.68	-0.20	-0.20	-0.16	-0.16	-0.02	-0.07	0.75	0.49	-0.11	-0.07	-0.01	0.02
Log Lab EC	-0.17	-0.55	-0.24	-0.21	-0.23	0.00	-0.08	0.74	0.70	-0.13	-0.08	-0.02	-0.02	0.02

APPENDIX E – r_p Values between All Constituents in the Upstream Ground Water (cont.)

	Se	Log Se	Fe	Log Fe	U	Log U	Fe-Trec	Log Fe-Trec	Lab pH	Log Lab pH	SAR	Log SAR	Adj SAR	Log Adj SAR	Lab EC	Log Lab EC
Ls	-0.19	-0.09	No Data	No Data	-0.24	-0.15	No Data	No Data	0.15	0.14	-0.18	-0.12	-0.01	0.12	-0.19	-0.17
Log Ls	-0.36	-0.12	No Data	No Data	-0.65	-0.39	No Data	No Data	0.16	0.15	-0.70	-0.50	-0.02	0.45	-0.68	-0.55
WT Depth	-0.08	-0.05	No Data	No Data	-0.19	-0.25	No Data	No Data	0.07	0.07	-0.22	-0.32	-0.16	-0.08	-0.20	-0.24
Log WT Depth	-0.05	-0.02	No Data	No Data	-0.18	-0.21	No Data	No Data	0.06	0.05	-0.21	-0.28	-0.12	-0.04	-0.20	-0.21
Field pH	-0.10	-0.08	No Data	No Data	-0.11	-0.13	No Data	No Data	0.77	0.77	-0.19	-0.22	-0.18	-0.08	-0.16	-0.24
Log Field pH	-0.10	-0.07	No Data	No Data	-0.10	-0.12	No Data	No Data	0.77	0.77	-0.19	-0.22	-0.19	-0.08	-0.16	-0.23
T	-0.01	0.01	No Data	No Data	-0.02	0.00	No Data	No Data	-0.05	-0.04	0.00	0.02	0.04	0.04	-0.02	0.00
Log T	-0.02	-0.02	No Data	No Data	-0.07	-0.06	No Data	No Data	-0.01	-0.01	-0.04	-0.04	0.03	0.04	-0.07	-0.08
Field EC	0.38	0.32	No Data	No Data	0.68	0.58	No Data	No Data	-0.11	-0.11	0.81	0.67	0.24	-0.24	0.75	0.74
Log Field EC	0.31	0.35	No Data	No Data	0.44	0.57	No Data	No Data	-0.15	-0.14	0.50	0.55	0.34	0.08	0.49	0.70
DO	0.01	0.20	No Data	No Data	-0.08	-0.10	No Data	No Data	0.13	0.13	-0.12	-0.20	-0.11	-0.10	-0.11	-0.13
Log DO	0.05	0.28	No Data	No Data	-0.01	-0.01	No Data	No Data	0.08	0.08	-0.08	-0.16	-0.10	-0.12	-0.07	-0.08
ORP	-0.04	0.16	No Data	No Data	-0.03	0.00	No Data	No Data	-0.23	-0.23	-0.01	-0.03	0.01	0.01	-0.01	-0.02
Log ORP	0.07	0.10	No Data	No Data	0.01	0.01	No Data	No Data	-0.26	-0.26	0.03	0.02	0.01	-0.03	0.02	0.02
Se	1.00	0.55	No Data	No Data	0.37	0.37	No Data	No Data	-0.11	-0.11	0.48	0.44	0.40	-0.06	0.31	0.39
Log Se	0.55	1.00	No Data	No Data	0.39	0.52	No Data	No Data	-0.15	-0.14	0.33	0.36	0.23	-0.01	0.28	0.40
Fe	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data							
Log Fe	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data							
U	0.37	0.39	No Data	No Data	1.00	0.76	No Data	No Data	-0.11	-0.10	0.79	0.61	0.13	-0.27	0.90	0.75
Log U	0.37	0.52	No Data	No Data	0.76	1.00	No Data	No Data	-0.10	-0.09	0.54	0.55	0.25	0.00	0.60	0.76
Fe-Trec	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data							
Log Fe-Trec	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data							
Lab pH	-0.11	-0.15	No Data	No Data	-0.11	-0.10	No Data	No Data	1.00	1.00	-0.16	-0.22	-0.19	-0.09	-0.14	-0.23
Log Lab pH	-0.11	-0.14	No Data	No Data	-0.10	-0.09	No Data	No Data	1.00	1.00	-0.16	-0.22	-0.19	-0.10	-0.13	-0.23
SAR	0.48	0.33	No Data	No Data	0.79	0.54	No Data	No Data	-0.16	1.00	0.86	0.39	-0.20	0.89	0.79	0.79
Log SAR	0.44	0.36	No Data	No Data	0.61	0.55	No Data	No Data	-0.22	0.86	1.00	0.58	0.16	0.71	0.81	0.81
Adj SAR	0.40	0.23	No Data	No Data	0.13	0.25	No Data	No Data	-0.19	0.39	0.58	1.00	0.75	0.14	0.40	0.40
Log Adj SAR	-0.06	-0.01	No Data	No Data	-0.27	0.00	No Data	No Data	-0.10	-0.20	0.16	0.75	1.00	-0.32	0.01	0.01
Lab EC	0.31	0.28	No Data	No Data	0.90	0.60	No Data	No Data	-0.14	0.89	0.71	0.14	-0.32	1.00	0.82	0.82
Log Lab EC	0.39	0.40	No Data	No Data	0.75	0.76	No Data	No Data	-0.23	0.79	0.81	0.40	0.01	0.82	1.00	1.00

APPENDIX E – r_p Values between All Constituents in the Upstream Ground Water (cont.)

	Na	Log Na	K	Log K	Ca	Log Ca	Mg	Log Mg	Hard	Log Hard	NO3	Log NO3	SO4	Log SO4	Cl	Log Cl	
LS	-0.19	-0.15	0.03	0.20	-0.12	-0.09	-0.19	-0.20	-0.18	-0.11	0.03	-0.20	-0.17	-0.02	0.00		
Log LS	-0.70	-0.54	0.05	0.15	-0.18	-0.16	-0.63	-0.55	-0.63	-0.50	-0.16	0.04	-0.69	-0.53	-0.46	-0.37	
WT Depth	-0.18	-0.30	-0.04	-0.04	-0.12	-0.09	-0.16	-0.26	-0.17	-0.19	-0.04	0.03	-0.17	-0.20	-0.20	-0.31	
Log WT Depth	-0.19	-0.26	-0.08	-0.08	-0.09	-0.06	-0.17	-0.22	-0.18	-0.16	-0.02	0.03	-0.17	-0.16	-0.22	-0.28	
Field pH	-0.14	-0.24	-0.09	-0.07	-0.24	-0.22	-0.11	-0.24	-0.15	-0.24	-0.15	0.02	-0.14	-0.22	-0.15	-0.21	
Log Field pH	-0.14	-0.24	-0.09	-0.07	-0.23	-0.21	-0.10	-0.23	-0.14	-0.23	-0.15	0.03	-0.14	-0.22	-0.14	-0.21	
T	-0.01	0.01	-0.03	-0.08	0.01	0.02	-0.02	-0.01	-0.02	0.00	0.04	0.07	-0.02	-0.01	0.02	0.05	
Log T	-0.05	-0.06	-0.02	-0.05	-0.07	-0.07	-0.07	-0.09	-0.08	-0.09	0.05	0.10	-0.08	-0.10	-0.02	-0.04	
Field EC	0.78	0.73	-0.04	-0.06	0.40	0.41	0.67	0.72	0.71	0.70	0.33	0.22	0.79	0.72	0.57	0.62	
Log Field EC	0.44	0.64	-0.02	-0.07	0.58	0.62	0.39	0.67	0.48	0.70	0.28	0.22	0.48	0.69	0.32	0.53	
DO	-0.10	-0.18	-0.02	-0.06	-0.01	-0.04	-0.11	-0.18	-0.10	-0.11	0.01	0.20	-0.09	-0.11	-0.05	-0.15	
Log DO	-0.07	-0.14	-0.03	-0.13	0.02	-0.03	-0.07	-0.12	-0.06	-0.07	0.06	0.25	-0.05	-0.06	-0.03	-0.15	
ORP	-0.01	-0.04	-0.03	-0.11	0.01	-0.02	-0.02	-0.04	-0.04	-0.02	-0.03	0.01	0.10	0.00	-0.02	-0.05	-0.02
Log ORP	0.02	0.01	0.02	0.00	0.00	-0.01	0.00	-0.01	0.00	-0.01	0.06	0.06	0.01	-0.03	0.06	0.09	
Se	0.33	0.43	0.00	-0.01	0.21	0.20	0.20	0.36	0.23	0.32	0.69	0.37	0.28	0.37	0.37	0.42	
Log Se	0.24	0.40	0.00	-0.14	0.30	0.29	0.20	0.42	0.25	0.38	0.47	0.65	0.26	0.41	0.26	0.32	
Fe	No Data	No Data	No Data	No Data	No Data	No Data	No Data										
Log Fe	No Data	No Data	No Data	No Data	No Data	No Data	No Data										
U	0.88	0.70	-0.11	-0.20	-0.34	0.62	0.63	0.52	0.80	0.61	0.78	0.25	0.23	0.58	0.76	0.39	0.50
Log U	0.52	0.67	-0.20	-0.34	0.62	0.36	0.87	0.76	0.89	0.72	0.17	0.08	0.89	0.72	0.57	0.52	
Fe-Trec	No Data	No Data	No Data	No Data	No Data	No Data	No Data										
Log Fe-Trec	No Data	No Data	No Data	No Data	No Data	No Data	No Data										
Lab pH	-0.11	-0.23	-0.05	-0.03	-0.23	-0.21	-0.08	-0.23	-0.13	-0.22	-0.12	0.00	-0.12	-0.22	-0.15	-0.21	
Log Lab pH	-0.10	-0.23	-0.06	-0.04	-0.23	-0.21	-0.08	-0.23	-0.12	-0.22	-0.12	0.00	-0.11	-0.22	-0.14	-0.21	
SAR	0.93	0.86	0.02	0.04	0.27	0.28	0.79	0.74	0.79	0.66	0.33	0.11	0.88	0.73	0.72	0.75	
Log SAR	0.70	0.96	0.05	0.06	0.34	0.37	0.58	0.78	0.61	0.66	0.32	0.14	0.67	0.76	0.62	0.83	
Adj SAR	0.14	0.53	0.05	0.07	0.29	0.31	-0.01	0.35	0.05	0.30	0.29	0.16	0.10	0.39	0.16	0.44	
Log Adj SAR	-0.37	0.11	0.03	0.02	0.12	0.16	-0.41	0.00	-0.32	-0.02	-0.01	0.07	-0.35	0.03	-0.36	0.02	
Lab EC	0.97	0.79	-0.02	-0.05	0.37	0.38	0.97	0.79	0.98	0.76	0.23	0.06	0.99	0.77	0.62	0.64	
Log Lab EC	0.73	0.93	0.00	-0.06	0.74	0.77	0.69	0.96	0.79	0.96	0.31	0.15	0.77	0.98	0.60	0.79	

APPENDIX E – r_p Values between All Constituents in the Upstream Ground Water (cont.)

	CO ₃	Log CO ₃	HCO ₃	Log HCO ₃	Alk	Log Alk	B	Log B	Cat/An	Log Cat/An	TDS	Log TDS
LS	No Data	-0.12	-0.13	-0.12	-0.13	-0.07	-0.20	-0.12	-0.12	-0.20	-0.18	
Log LS	No Data	-0.51	-0.41	-0.51	-0.41	-0.28	-0.54	-0.09	-0.09	-0.69	-0.56	
WT Depth	-0.03	-0.03	-0.23	-0.25	-0.23	-0.02	-0.20	-0.07	-0.08	-0.18	-0.22	
Log WT Depth	-0.03	-0.03	-0.24	-0.26	-0.24	-0.26	0.00	-0.16	-0.07	-0.08	-0.19	
Field pH	-0.06	-0.06	-0.14	-0.10	-0.14	-0.10	-0.09	-0.24	-0.07	-0.07	-0.15	
Log Field pH	-0.05	-0.05	-0.13	-0.09	-0.13	-0.09	-0.09	-0.24	-0.07	-0.08	-0.15	
T	-0.01	-0.01	0.06	0.06	0.06	0.06	0.00	-0.03	0.01	0.02	-0.01	
Log T	-0.01	-0.01	0.01	0.00	0.01	0.00	0.03	-0.03	0.04	0.06	-0.07	
Field EC	-0.03	-0.03	0.58	0.45	0.58	0.45	0.25	0.63	0.05	0.08	0.75	
Log Field EC	-0.03	-0.03	0.39	0.37	0.39	0.37	0.13	0.56	0.15	0.20	0.48	
DO	-0.05	-0.05	-0.26	-0.26	-0.26	-0.26	0.00	-0.10	-0.04	-0.04	-0.10	
Log DO	-0.06	-0.06	-0.27	-0.24	-0.27	-0.24	0.02	0.00	-0.03	-0.02	-0.07	
ORP	0.03	0.03	-0.20	-0.23	-0.20	-0.23	0.01	0.06	0.08	0.10	-0.02	
Log ORP	0.02	0.02	-0.08	-0.11	-0.08	-0.11	0.00	0.03	0.12	0.16	0.01	
Se	0.00	0.00	0.15	0.18	0.15	0.18	0.50	0.45	0.05	0.07	0.30	
Log Se	0.03	0.03	0.00	0.04	0.00	0.04	0.15	0.42	0.11	0.12	0.26	
Fe	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	
Log Fe	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	
U	-0.03	-0.03	0.55	0.47	0.55	0.47	0.21	0.64	0.09	0.12	0.90	
Log U	-0.06	-0.06	0.42	0.53	0.42	0.53	0.14	0.67	0.08	0.13	0.59	
Fe-Trec	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	
Log Fe-Trec	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	
Lab pH	-0.05	-0.05	-0.02	0.02	-0.02	0.02	-0.05	-0.22	-0.09	-0.11	-0.12	
Log Lab pH	-0.05	-0.05	-0.02	0.03	-0.02	0.03	-0.05	-0.21	-0.09	-0.11	-0.12	
SAR	-0.02	-0.02	0.61	0.46	0.61	0.46	0.39	0.72	0.07	0.08	0.90	
Log SAR	-0.03	-0.03	0.52	0.44	0.52	0.44	0.21	0.73	0.07	0.09	0.69	
Adj SAR	-0.03	-0.03	0.10	0.13	0.10	0.13	0.56	0.57	0.04	0.06	0.12	
Log Adj SAR	-0.01	-0.01	-0.19	-0.09	-0.19	-0.09	0.15	0.16	0.04	0.05	-0.35	
Lab EC	-0.03	-0.03	0.64	0.48	0.64	0.48	0.18	0.64	0.10	0.12	0.99	
Log Lab EC	-0.06	-0.06	0.55	0.48	0.56	0.48	0.16	0.79	0.11	0.15	0.79	

APPENDIX E – r_p Values between All Constituents in the Upstream Ground Water (cont.)

	Ls	Log Ls	WT Depth	Log WT Depth	Field pH	Log Field pH	T	Log T	Field EC	Log Field EC	DO	Log DO	ORP	Log ORP
Na	-0.19	-0.70	-0.18	-0.19	-0.14	-0.01	-0.05	0.78	0.44	-0.10	-0.07	-0.01	0.02	
Log Na	-0.15	-0.54	-0.30	-0.26	-0.24	0.01	-0.06	0.73	0.64	-0.18	-0.14	-0.04	0.01	
K	0.03	0.05	-0.04	-0.08	-0.09	-0.03	-0.02	-0.04	-0.02	-0.02	-0.03	-0.03	0.02	
Log K	0.20	0.15	-0.04	-0.08	-0.07	-0.08	-0.05	-0.06	-0.07	-0.06	-0.13	-0.11	0.00	
Ca	-0.12	-0.18	-0.12	-0.09	-0.24	-0.23	0.01	-0.07	0.40	0.58	-0.01	0.02	0.01	0.00
Log Ca	-0.09	-0.16	-0.09	-0.06	-0.22	-0.21	0.02	-0.07	0.41	0.62	-0.04	-0.03	-0.02	-0.01
Mg	-0.19	-0.63	-0.16	-0.17	-0.11	-0.10	-0.02	-0.07	0.67	0.39	-0.11	-0.07	-0.02	0.00
Log Mg	-0.19	-0.55	-0.26	-0.22	-0.24	-0.23	-0.01	-0.09	0.72	0.67	-0.18	-0.12	-0.04	-0.01
Hard	-0.20	-0.63	-0.17	-0.18	-0.15	-0.14	-0.02	-0.08	0.71	0.48	-0.10	-0.06	-0.02	0.00
Log Hard	-0.18	-0.50	-0.19	-0.16	-0.24	-0.23	0.00	-0.09	0.70	0.70	-0.11	-0.07	-0.03	-0.01
NO3	-0.11	-0.16	-0.04	-0.02	-0.15	-0.15	0.04	0.05	0.33	0.28	0.01	0.06	0.01	0.06
Log NO3	0.03	0.04	0.03	0.03	0.02	0.03	0.07	0.10	0.22	0.22	0.20	0.25	0.10	0.06
SO4	-0.20	-0.69	-0.17	-0.17	-0.14	-0.14	-0.02	-0.08	0.79	0.48	-0.09	-0.05	0.00	0.01
Log SO4	-0.17	-0.53	-0.20	-0.16	-0.22	-0.22	-0.01	-0.10	0.72	0.69	-0.11	-0.06	-0.02	-0.03
Cl	-0.02	-0.46	-0.20	-0.22	-0.15	-0.14	0.02	-0.02	0.57	0.32	-0.05	-0.03	-0.05	0.06
Log Cl	0.00	-0.37	-0.31	-0.28	-0.21	-0.21	0.05	-0.04	0.62	0.53	-0.15	-0.15	-0.02	0.09
CO3	No Data	No Data	-0.03	-0.03	-0.06	-0.05	-0.01	-0.01	-0.03	-0.03	-0.05	-0.06	0.03	0.02
Log CO3	No Data	No Data	-0.03	-0.03	-0.06	-0.05	-0.01	-0.01	-0.03	-0.03	-0.05	-0.06	0.03	0.02
HCO3	-0.12	-0.51	-0.23	-0.24	-0.14	-0.13	0.06	0.01	0.58	0.39	-0.26	-0.27	-0.20	-0.08
Log HCO3	-0.13	-0.41	-0.25	-0.26	-0.10	-0.09	0.06	0.00	0.45	0.37	-0.26	-0.24	-0.23	-0.11
Alk	-0.12	-0.51	-0.23	-0.24	-0.14	-0.13	0.06	0.01	0.58	0.39	-0.26	-0.27	-0.20	-0.08
Log Alk	-0.13	-0.41	-0.25	-0.26	-0.10	-0.09	0.06	0.00	0.45	0.37	-0.26	-0.24	-0.23	-0.11
B	-0.07	-0.28	-0.02	0.00	-0.09	-0.09	0.00	0.03	0.25	0.13	0.00	0.02	0.01	0.00
Log B	-0.20	-0.54	-0.20	-0.16	-0.24	-0.24	-0.03	-0.03	0.63	0.56	-0.10	0.00	0.06	0.03
Cat/An	-0.12	-0.09	-0.07	-0.07	-0.07	-0.07	0.01	0.04	0.05	0.15	-0.04	-0.03	0.08	0.12
Log Cat/An	-0.12	-0.09	-0.08	-0.08	-0.07	-0.08	0.02	0.06	0.08	0.20	-0.04	-0.02	0.10	0.16
TDS	-0.20	-0.69	-0.18	-0.19	-0.15	-0.15	-0.01	-0.07	0.79	0.48	-0.10	-0.07	-0.02	0.01
Log TDS	-0.18	-0.56	-0.22	-0.19	-0.24	-0.24	0.00	-0.08	0.75	0.70	-0.13	-0.09	-0.04	-0.02

APPENDIX E- r_p Values between All Constituents in the Upstream Ground Water (cont.)

	Se	Log Se	Fe	Log Fe	U	Log U	Fe/Trec	Log Fe/Trec	Lab pH	Log Lab pH	SAR	Log SAR	Adj SAR	Log Adj SAR	Lab EC	Log Lab EC
Na	0.33	0.24	No Data	No Data	0.88	0.52	No Data	No Data	-0.11	-0.10	0.93	0.70	0.14	-0.37	0.97	0.73
Log Na	0.43	0.40	No Data	No Data	0.70	0.67	No Data	No Data	-0.23	-0.23	0.86	0.96	0.53	0.11	0.79	0.93
K	0.00	0.00	No Data	No Data	-0.11	-0.20	No Data	No Data	-0.05	-0.06	0.02	0.05	0.05	0.03	-0.02	0.00
Log K	-0.01	-0.14	No Data	No Data	-0.20	-0.34	No Data	No Data	-0.03	-0.04	0.04	0.04	0.06	0.07	0.02	-0.05
Ca	0.21	0.30	No Data	No Data	0.36	0.62	No Data	No Data	-0.23	-0.23	0.27	0.34	0.29	0.12	0.37	0.74
Log Ca	0.20	0.29	No Data	No Data	0.36	0.63	No Data	No Data	-0.21	-0.21	0.28	0.37	0.31	0.16	0.38	0.77
Mg	0.20	0.20	No Data	No Data	0.87	0.52	No Data	No Data	-0.08	-0.08	0.79	0.58	-0.01	-0.41	0.97	0.69
Log Mg	0.36	0.42	No Data	No Data	0.76	0.80	No Data	No Data	-0.23	-0.23	0.74	0.78	0.35	0.00	0.79	0.96
Hard	0.23	0.25	No Data	No Data	0.89	0.61	No Data	No Data	-0.13	-0.12	0.79	0.61	0.05	-0.32	0.98	0.79
Log Hard	0.32	0.38	No Data	No Data	0.72	0.78	No Data	No Data	-0.22	-0.22	0.66	0.66	0.30	-0.02	0.76	0.96
NO3	0.69	0.47	No Data	No Data	0.17	0.25	No Data	No Data	-0.12	-0.12	0.33	0.32	0.29	-0.01	0.23	0.31
Log NO3	0.37	0.65	No Data	No Data	0.08	0.23	No Data	No Data	0.00	0.00	0.11	0.14	0.16	0.07	0.06	0.15
SO4	0.28	0.26	No Data	No Data	0.89	0.58	No Data	No Data	-0.12	-0.11	0.88	0.67	0.10	-0.35	0.99	0.77
Log SO4	0.37	0.41	No Data	No Data	0.72	0.76	No Data	No Data	-0.22	-0.22	0.73	0.76	0.39	0.03	0.77	0.98
Cl	0.37	0.26	No Data	No Data	0.57	0.39	No Data	No Data	-0.15	-0.14	0.72	0.62	0.16	-0.36	0.62	0.60
Log Cl	0.42	0.32	No Data	No Data	0.52	0.50	No Data	No Data	-0.21	-0.21	0.75	0.83	0.44	0.02	0.64	0.79
CO3	0.00	0.03	No Data	No Data	-0.03	-0.06	No Data	No Data	-0.05	-0.05	-0.02	-0.03	-0.03	-0.01	-0.03	-0.06
Log CO3	0.00	0.03	No Data	No Data	-0.03	-0.06	No Data	No Data	-0.05	-0.05	-0.02	-0.03	-0.03	-0.01	-0.03	-0.06
HCO3	0.15	0.00	No Data	No Data	0.55	0.42	No Data	No Data	-0.02	-0.02	0.61	0.52	0.10	-0.19	0.64	0.55
Log HCO3	0.18	0.04	No Data	No Data	0.47	0.53	No Data	No Data	0.02	0.03	0.46	0.44	0.13	-0.09	0.48	0.48
Alk	0.15	0.00	No Data	No Data	0.55	0.42	No Data	No Data	-0.02	-0.02	0.61	0.52	0.10	-0.19	0.64	0.56
Log Alk	0.18	0.04	No Data	No Data	0.47	0.53	No Data	No Data	0.02	0.03	0.46	0.44	0.13	-0.09	0.48	0.48
B	0.50	0.15	No Data	No Data	0.21	0.14	No Data	No Data	-0.05	-0.05	0.39	0.21	0.56	0.15	0.18	0.16
Log B	0.45	0.42	No Data	No Data	0.64	0.67	No Data	No Data	-0.22	-0.21	0.72	0.73	0.57	0.16	0.64	0.79
Cat/An	0.05	0.11	No Data	No Data	0.09	0.08	No Data	No Data	-0.09	-0.09	0.07	0.07	0.04	0.04	0.10	0.11
Log Cat/An	0.07	0.12	No Data	No Data	0.12	0.13	No Data	No Data	-0.11	-0.11	0.08	0.09	0.06	0.05	0.12	0.15
TDS	0.30	0.26	No Data	No Data	0.90	0.59	No Data	No Data	-0.12	-0.12	0.90	0.69	0.12	-0.35	0.99	0.79
Log TDS	0.39	0.40	No Data	No Data	0.75	0.77	No Data	No Data	-0.22	-0.22	0.79	0.80	0.40	0.00	0.81	0.99

APPENDIX E – r_p Values between All Constituents in the Upstream Ground Water (cont.)

	Na	Log Na	K	Log K	Ca	Log Ca	Mg	Log Mg	Hard	Log Hard	NO3	Log NO3	SO4	Log SO4	Cl	Log Cl
Na	1.00	0.74	-0.01	-0.02	0.22	0.23	0.95	0.70	0.93	0.64	0.24	0.07	0.98	0.67	0.65	0.61
Log Na	0.74	1.00	0.02	0.00	0.54	0.57	0.65	0.90	0.72	0.83	0.33	0.16	0.74	0.89	0.63	0.84
K	-0.01	0.02	1.00	0.69	-0.04	-0.02	-0.04	-0.05	-0.05	-0.04	0.07	0.03	-0.03	-0.02	0.07	0.09
Log K	-0.02	0.00	0.69	1.00	-0.13	-0.10	-0.07	-0.12	-0.09	-0.12	0.04	-0.05	-0.05	-0.07	-0.08	0.11
Ca	0.22	0.54	-0.04	-0.13	1.00	0.97	0.24	0.69	0.43	0.84	0.21	0.13	0.33	0.79	0.28	0.45
Log Ca	0.23	0.57	-0.02	-0.10	0.97	1.00	0.24	0.71	0.43	0.87	0.21	0.14	0.34	0.81	0.27	0.49
Mg	0.95	0.65	-0.04	-0.07	0.24	0.24	1.00	0.69	0.98	0.65	0.15	0.03	0.97	0.64	0.52	0.49
Log Mg	0.70	0.90	-0.05	-0.12	0.69	0.71	0.69	1.00	0.79	0.95	0.28	0.14	0.76	0.95	0.55	0.72
Hard	0.93	0.72	-0.05	-0.09	0.43	0.43	0.98	0.79	1.00	0.78	0.18	0.05	0.97	0.76	0.54	0.55
Log Hard	0.64	0.83	-0.04	-0.12	0.84	0.87	0.65	0.95	0.78	1.00	0.27	0.15	0.73	0.97	0.51	0.68
NO3	0.24	0.33	0.07	0.04	0.21	0.21	0.15	0.28	0.18	0.27	1.00	0.66	0.21	0.30	0.21	0.31
Log NO3	0.07	0.16	0.03	-0.05	0.13	0.14	0.03	0.14	0.05	0.15	0.66	1.00	0.08	0.17	0.00	0.09
SO4	0.98	0.74	-0.03	-0.07	0.33	0.34	0.97	0.76	0.97	0.73	0.21	0.08	1.00	0.74	0.58	0.58
Log SO4	0.67	0.89	-0.02	-0.08	0.79	0.81	0.64	0.95	0.76	0.97	0.30	0.17	0.74	1.00	0.53	0.73
Cl	0.65	0.53	0.07	0.11	0.28	0.27	0.52	0.55	0.54	0.51	0.21	0.00	0.58	0.53	1.00	0.79
Log Cl	0.61	0.84	0.09	0.13	0.45	0.49	0.49	0.72	0.55	0.68	0.31	0.09	0.58	0.73	0.79	1.00
CO3	-0.02	-0.04	0.00	0.03	-0.07	-0.07	-0.02	-0.05	-0.03	-0.06	-0.02	0.00	-0.04	-0.13	-0.03	-0.12
Log CO3	-0.02	-0.04	0.00	0.03	-0.07	-0.07	-0.02	-0.05	-0.03	-0.06	-0.02	0.00	-0.04	-0.13	-0.03	-0.12
HCO3	0.64	0.56	-0.01	0.00	0.24	0.27	0.61	0.54	0.62	0.52	0.11	-0.07	0.62	0.47	0.47	0.55
Log HCO3	0.47	0.48	-0.04	-0.05	0.26	0.31	0.44	0.46	0.46	0.46	0.14	0.01	0.45	0.41	0.39	0.49
Alk	0.64	0.56	-0.01	0.00	0.24	0.27	0.61	0.54	0.62	0.52	0.11	-0.07	0.62	0.47	0.47	0.55
Log Alk	0.47	0.48	-0.04	-0.05	0.26	0.31	0.44	0.46	0.46	0.46	0.14	0.01	0.45	0.41	0.39	0.49
B	0.27	0.19	0.01	0.04	0.03	0.04	0.09	0.13	0.09	0.11	0.28	0.12	0.20	0.16	0.21	0.18
Log B	0.60	0.79	-0.02	-0.11	0.52	0.53	0.51	0.79	0.59	0.73	0.31	0.19	0.62	0.77	0.43	0.58
Cat/An	0.08	0.12	-0.01	-0.04	0.10	0.12	0.09	0.11	0.11	0.13	0.02	0.03	0.06	0.02	0.00	-0.02
Log Cat/An	0.10	0.15	-0.02	-0.05	0.14	0.17	0.11	0.15	0.13	0.17	0.03	0.05	0.08	0.06	0.01	0.01
TDS	0.98	0.76	-0.03	-0.05	0.34	0.35	0.97	0.77	0.97	0.73	0.23	0.07	1.00	0.74	0.63	0.62
Log TDS	0.72	0.92	-0.01	-0.06	0.75	0.78	0.68	0.96	0.79	0.97	0.32	0.16	0.78	0.99	0.60	0.77

APPENDIX E $-r_p$ Values between All Constituents in the Upstream Ground Water (cont.)

	CO3	Log CO3	HCO3	Log HCO3	Alk	Log Alk	B	Log B	Cat/An	Log Cat/An	TDS	Log TDS
Na	-0.02	-0.02	0.64	0.47	0.64	0.47	0.27	0.60	0.08	0.10	0.98	0.72
Log Na	-0.04	-0.04	0.56	0.48	0.56	0.48	0.19	0.79	0.12	0.15	0.76	0.92
K	0.00	0.00	-0.01	-0.04	-0.01	-0.04	0.01	-0.02	-0.01	-0.02	-0.03	-0.01
Log K	0.03	0.03	0.00	-0.05	0.00	-0.05	0.04	-0.11	-0.04	-0.05	-0.05	-0.06
Ca	-0.07	-0.07	0.24	0.26	0.24	0.26	0.03	0.52	0.10	0.14	0.34	0.75
Log Ca	-0.07	-0.07	0.27	0.31	0.27	0.31	0.04	0.53	0.12	0.17	0.35	0.78
Mg	-0.02	-0.02	0.61	0.44	0.61	0.44	0.09	0.51	0.09	0.11	0.97	0.68
Log Mg	-0.05	-0.05	0.54	0.46	0.54	0.46	0.13	0.79	0.11	0.15	0.77	0.96
Hard	-0.03	-0.03	0.62	0.46	0.62	0.46	0.09	0.59	0.11	0.13	0.97	0.79
Log Hard	-0.06	-0.06	0.52	0.46	0.52	0.46	0.11	0.73	0.13	0.17	0.73	0.97
NO3	-0.02	-0.02	0.11	0.14	0.11	0.14	0.28	0.31	0.02	0.03	0.23	0.32
Log NO3	0.00	0.00	-0.07	0.01	-0.07	0.01	0.12	0.19	0.03	0.05	0.07	0.16
SO4	-0.04	-0.04	0.62	0.45	0.62	0.45	0.20	0.62	0.06	0.08	1.00	0.78
Log SO4	-0.13	-0.13	0.47	0.41	0.47	0.41	0.16	0.77	0.02	0.06	0.74	0.99
Cl	-0.03	-0.03	0.47	0.39	0.47	0.39	0.21	0.43	0.00	0.01	0.63	0.60
Log Cl	-0.12	-0.12	0.55	0.49	0.55	0.49	0.18	0.58	-0.02	0.01	0.62	0.77
CO3	1.00	1.00	-0.05	-0.06	-0.05	-0.06	0.00	-0.05	0.66	0.51	-0.03	-0.09
Log CO3	1.00	1.00	-0.05	-0.06	-0.05	-0.06	0.00	-0.05	0.66	0.51	-0.03	-0.09
HCO3	-0.05	-0.05	1.00	0.90	1.00	0.90	0.08	0.37	-0.08	-0.08	0.66	0.58
Log HCO3	-0.06	-0.06	0.90	1.00	0.90	1.00	0.09	0.34	-0.07	-0.07	0.49	0.51
Alk	-0.05	-0.05	1.00	0.90	1.00	0.90	0.08	0.37	-0.07	-0.08	0.66	0.58
Log Alk	-0.06	-0.06	0.90	1.00	0.90	1.00	0.09	0.34	-0.07	-0.07	0.49	0.51
B	0.00	0.00	0.08	0.09	0.08	0.09	1.00	0.50	-0.01	-0.01	0.21	0.18
Log B	-0.05	-0.05	0.37	0.34	0.37	0.34	0.50	1.00	0.11	0.16	0.62	0.78
Cat/An	0.66	0.66	-0.08	-0.07	-0.07	-0.07	-0.01	0.11	1.00	0.98	0.07	0.05
Log Cat/An	0.51	0.51	-0.08	-0.07	-0.08	-0.07	-0.01	0.16	0.98	1.00	0.08	0.09
TDS	-0.03	-0.03	0.66	0.49	0.66	0.49	0.21	0.62	0.07	0.08	1.00	0.79
Log TDS	-0.09	-0.09	0.58	0.51	0.58	0.51	0.18	0.78	0.05	0.09	0.79	1.00

APPENDIX F – r_p Values between All Constituents in the Downstream Ground Water

	Ls	Log Ls	WT Depth	Log WT Depth	Field pH	Log Field pH	T	Log T	Field EC	Log	DO	Log DO	ORP	Log ORP
Ls	1.00	0.95	-0.03	-0.16	-0.01	-0.01	0.02	0.00	0.18	0.13	-0.07	-0.16	0.03	0.00
Log Ls	0.95	1.00	-0.02	-0.13	0.04	0.04	0.04	0.03	0.10	0.07	-0.05	-0.15	-0.01	-0.03
WT Depth	-0.03	0.02	1.00	0.75	-0.01	-0.01	0.09	0.01	-0.03	-0.07	0.15	0.17	0.00	0.07
Log WT Depth	-0.16	-0.13	0.75	1.00	-0.05	-0.05	0.08	0.08	0.01	-0.02	0.31	0.35	0.08	0.10
Field pH	-0.01	0.04	-0.01	-0.05	1.00	1.00	-0.04	-0.06	-0.17	-0.17	0.08	0.05	-0.03	-0.03
Log Field pH	-0.01	0.04	-0.01	-0.05	1.00	1.00	-0.04	-0.06	-0.17	-0.16	0.07	0.05	-0.04	-0.03
T	0.02	0.04	0.09	0.08	-0.04	-0.04	1.00	0.55	0.07	0.06	-0.02	-0.03	0.03	0.02
Log T	0.00	0.03	0.01	0.08	-0.06	-0.06	0.55	1.00	0.03	0.02	-0.01	-0.02	-0.13	-0.14
Field EC	0.18	0.10	-0.03	0.01	-0.17	-0.17	0.07	0.03	1.00	0.86	-0.06	-0.02	0.01	0.00
Log Field EC	0.13	0.07	-0.07	-0.02	-0.17	-0.16	0.06	0.02	0.86	1.00	-0.11	-0.06	0.00	0.02
DO	-0.07	-0.05	0.15	0.31	0.08	0.07	-0.02	-0.01	-0.06	-0.11	1.00	0.85	0.24	0.19
Log DO	-0.16	-0.15	0.17	0.35	0.05	0.05	-0.03	-0.02	-0.02	-0.06	0.85	1.00	0.30	0.26
ORP	0.03	-0.01	0.00	0.08	-0.03	-0.04	0.03	-0.13	0.01	0.00	0.24	0.30	1.00	0.88
Log ORP	0.00	-0.03	0.07	0.10	-0.03	-0.03	0.02	-0.14	0.00	0.02	0.19	0.26	0.88	1.00
Se	0.18	0.05	0.00	0.04	-0.21	-0.22	0.00	0.01	0.47	0.32	0.02	0.05	0.09	0.08
Log Se	0.11	-0.02	0.05	0.12	-0.21	-0.22	0.01	-0.05	0.48	0.46	0.16	0.22	0.26	0.14
Fe	-0.06	-0.03	0.11	0.10	0.02	0.02	0.09	0.08	0.01	0.03	-0.10	-0.09	-0.43	-0.37
Log Fe	0.07	0.08	-0.03	-0.06	-0.12	-0.12	0.20	0.18	0.16	0.19	-0.11	-0.12	-0.60	-0.39
U	0.09	0.12	0.06	0.12	-0.01	-0.02	0.18	0.11	0.67	0.49	0.02	0.07	0.14	0.11
Log U	0.11	0.12	0.04	0.08	-0.01	-0.03	0.13	0.02	0.59	0.57	-0.06	0.01	0.20	0.12
Fe-Trec	-0.31	-0.32	0.22	0.24	0.01	0.01	0.07	0.08	-0.04	-0.13	0.14	0.18	-0.15	-0.20
Log Fe-Trec	-0.20	-0.15	0.40	0.42	-0.05	-0.05	0.14	0.15	0.11	0.04	0.32	0.36	-0.16	-0.16
Lab pH	-0.02	0.03	-0.20	-0.20	0.53	0.55	-0.05	-0.09	-0.08	-0.08	0.07	0.07	0.06	-0.04
Log Lab pH	-0.02	0.03	-0.20	-0.20	0.53	0.56	-0.05	-0.09	-0.08	-0.08	0.07	0.07	0.06	-0.04
SAR	0.30	0.23	0.01	0.01	-0.11	-0.12	0.07	0.03	0.85	0.73	-0.04	0.01	0.00	0.01
Log SAR	0.29	0.22	-0.01	-0.02	-0.13	-0.12	0.06	0.01	0.74	0.78	-0.06	-0.01	0.01	0.03
Adj SAR	0.26	0.20	-0.04	-0.04	-0.16	-0.16	-0.06	-0.02	0.58	0.63	-0.08	-0.04	-0.02	-0.02
Log Adj SAR	0.24	0.18	-0.11	-0.11	-0.11	-0.11	-0.19	-0.09	0.09	0.26	-0.05	-0.03	-0.04	-0.02
Lab EC	0.16	0.08	0.02	0.04	-0.13	-0.13	0.09	0.02	0.90	0.73	-0.04	0.00	0.02	0.03
Log Lab EC	0.13	0.07	0.01	0.03	-0.16	-0.16	0.08	0.02	0.80	0.85	-0.11	-0.05	0.03	0.07

APPENDIX F – r_p Values between All Constituents in the Downstream Ground Water (cont.)

	Se	Log Se	Fe	Log Fe	U	Log U	Fe-Trec	Log Fe-Trec	Lab pH	Log Lab	SAR	Log SAR	Adj SAR	Log Adj SAR	Lab EC	Log Lab
LS	0.18	0.11	-0.06	0.07	0.09	0.11	-0.31	-0.20	-0.02	0.30	0.29	0.26	0.24	0.16	0.13	
Log LS	0.05	-0.02	-0.03	0.08	0.12	0.12	-0.32	-0.15	0.03	0.23	0.22	0.20	0.18	0.08	0.07	
WT Depth	0.00	0.05	0.11	-0.03	0.06	0.04	0.22	0.40	-0.20	-0.01	-0.01	-0.04	-0.11	0.02	0.01	
Log WT Depth	0.04	0.12	0.10	-0.06	0.12	0.08	0.24	0.42	-0.20	0.01	-0.02	-0.04	-0.11	0.04	0.03	
Field pH	-0.21	0.02	-0.12	-0.01	-0.01	0.01	-0.05	0.53	0.53	-0.11	-0.13	-0.16	-0.11	-0.13	-0.16	
Log Field pH	-0.22	0.02	-0.12	-0.02	-0.03	0.01	-0.05	0.55	0.56	-0.12	-0.12	-0.16	-0.11	-0.13	-0.16	
T	0.00	0.01	0.09	0.20	0.18	0.13	0.07	0.14	-0.05	-0.05	0.07	0.06	-0.06	-0.19	0.09	0.08
Log T	0.01	-0.05	0.08	0.18	0.11	0.02	0.08	0.15	-0.09	-0.09	0.03	0.01	-0.02	-0.09	0.02	0.02
Field EC	0.47	0.48	0.01	0.16	0.67	0.59	-0.04	0.11	-0.08	-0.08	0.85	0.74	0.58	0.09	0.90	0.80
Log Field EC	0.32	0.46	0.03	0.19	0.49	0.57	-0.13	0.04	-0.07	-0.07	0.73	0.78	0.63	0.26	0.73	0.85
DO	0.02	0.16	-0.10	-0.11	0.02	-0.06	0.14	0.32	0.07	0.07	-0.04	-0.06	-0.08	-0.05	-0.04	-0.11
Log DO	0.05	0.22	-0.09	-0.12	0.07	0.01	0.18	0.36	0.06	0.06	0.01	-0.01	-0.04	-0.03	0.00	-0.05
ORP	0.09	0.26	-0.43	-0.60	0.14	0.20	-0.15	-0.16	0.03	0.02	0.00	0.01	-0.04	-0.04	0.02	0.03
Log ORP	0.08	0.14	-0.37	-0.39	0.11	0.12	-0.20	-0.16	-0.04	-0.04	0.01	0.03	-0.02	-0.02	0.03	0.07
Se	1.00	0.41	-0.02	0.09	0.73	0.58	0.00	0.07	-0.17	-0.18	0.35	0.28	0.28	0.09	0.41	0.33
Log Se	0.41	1.00	-0.11	-0.03	0.47	0.52	0.11	0.12	-0.10	-0.10	0.50	0.51	0.38	0.10	0.49	0.52
Fe	-0.02	-0.11	1.00	0.52	No Data	No Data	-0.45	-0.34	-0.05	-0.05	0.10	0.13	0.10	0.12	0.07	0.07
Log Fe	0.09	-0.03	0.52	1.00	No Data	No Data	-0.81	-0.94	-0.15	-0.15	0.18	0.15	0.17	0.12	0.13	0.10
U	0.73	0.47	No Data	No Data	1.00	0.83	No Data	No Data	0.01	0.01	0.71	0.53	-0.01	-0.44	0.83	0.68
Log U	0.58	0.52	No Data	No Data	0.83	1.00	No Data	No Data	-0.06	-0.06	0.56	0.51	0.16	-0.20	0.69	0.72
Fe-Trec	0.00	0.11	-0.45	-0.81	No Data	No Data	1.00	0.73	-0.01	0.00	0.11	0.12	0.15	0.15	-0.01	-0.09
Log Fe-Trec	0.07	0.12	-0.34	-0.94	No Data	No Data	0.73	1.00	-0.07	0.21	0.16	0.21	0.21	0.17	0.15	0.10
Lab pH	-0.17	-0.10	-0.05	-0.15	0.01	-0.06	-0.01	-0.07	1.00	1.00	-0.07	-0.10	-0.07	-0.05	-0.05	-0.06
Log Lab pH	-0.18	-0.10	-0.05	-0.15	0.01	-0.06	0.00	-0.07	1.00	1.00	-0.06	-0.10	-0.07	-0.05	-0.05	-0.06
SAR	0.35	0.50	0.10	0.18	0.71	0.56	0.11	0.21	-0.07	-0.05	1.00	0.92	0.69	0.09	0.92	0.86
Log SAR	0.28	0.51	0.13	0.15	0.53	0.51	0.12	0.16	-0.06	-0.06	0.92	1.00	0.75	0.27	0.79	0.88
Adj SAR	0.28	0.38	0.10	0.17	-0.01	0.16	0.15	0.21	-0.10	-0.10	0.69	0.75	1.00	0.76	0.53	0.65
Log Adj SAR	0.09	0.10	0.12	0.12	-0.44	-0.20	0.15	0.17	-0.07	-0.07	0.99	0.27	0.76	1.00	-0.03	0.17
Lab EC	0.41	0.49	0.07	0.13	0.83	0.69	-0.01	0.15	-0.05	-0.05	0.92	0.79	0.53	-0.03	1.00	0.89
Log Lab EC	0.33	0.52	0.07	0.10	0.68	0.72	-0.09	0.10	-0.06	-0.06	0.86	0.88	0.65	0.17	0.89	1.00

APPENDIX F – r_p Values between All Constituents in the Downstream Ground Water (cont.)

	Na	Log Na	K	Log K	Ca	Log Ca	Mg	Log Mg	Hard	Log	NO ₃	Log NO ₃	SO ₄	Log SO ₄	Cl	Log Cl
LS	0.24	0.22	-0.13	-0.23	-0.19	-0.17	0.21	0.21	0.05	0.03	0.08	0.07	0.14	0.10	0.09	0.10
Log LS	0.16	0.15	-0.07	-0.17	-0.23	-0.21	0.14	0.14	-0.01	-0.03	0.07	0.02	0.06	0.03	0.03	0.05
WT Depth	0.01	-0.01	-0.02	0.00	0.05	0.03	-0.01	-0.06	0.01	0.00	-0.01	0.06	0.02	0.00	0.00	0.01
Log WT Depth	0.02	0.00	0.01	0.08	0.09	0.05	0.03	-0.02	0.06	0.05	0.02	0.11	0.07	0.04	-0.03	0.00
Field pH	-0.11	-0.15	-0.09	-0.12	-0.23	-0.19	-0.11	-0.14	-0.16	-0.19	-0.18	-0.17	-0.14	-0.17	-0.07	-0.16
Log Field pH	-0.11	-0.15	-0.08	-0.11	-0.23	-0.19	-0.12	-0.14	-0.16	-0.19	-0.20	-0.17	-0.14	-0.17	-0.07	-0.16
T	0.07	0.07	0.04	0.07	0.04	0.03	0.08	0.08	0.08	0.07	0.00	0.01	0.08	0.06	0.06	0.10
Log T	0.03	0.02	0.04	0.05	-0.01	-0.03	0.06	0.05	0.04	0.02	-0.03	-0.02	0.05	0.02	0.01	0.04
Field EC	0.89	0.76	0.09	0.24	0.45	0.36	0.85	0.75	0.86	0.73	0.38	0.29	0.80	0.68	0.76	0.75
Log Field EC	0.69	0.82	0.12	0.32	0.61	0.51	0.67	0.80	0.76	0.81	0.25	0.30	0.74	0.78	0.44	0.75
DO	-0.03	-0.08	-0.11	-0.14	-0.17	-0.15	-0.02	-0.09	-0.07	-0.13	0.01	0.16	-0.04	-0.08	0.00	-0.12
Log DO	0.02	-0.02	-0.09	-0.05	-0.12	-0.11	0.02	-0.04	-0.02	-0.06	0.03	0.20	0.02	-0.01	0.00	-0.10
ORP	0.00	0.01	-0.11	-0.06	0.03	0.02	0.04	0.03	0.04	0.08	0.21	0.03	0.07	0.01	0.03	
Log ORP	0.00	0.05	0.08	0.11	0.10	0.08	0.01	0.05	0.05	0.08	0.07	0.15	0.04	0.08	0.01	0.09
Se	0.38	0.29	-0.01	0.03	0.16	0.11	0.43	0.32	0.41	0.30	0.97	0.35	0.30	0.23	0.38	0.32
Log Se	0.47	0.50	-0.03	0.11	0.31	0.24	0.47	0.49	0.50	0.47	0.31	0.69	0.50	0.46	0.29	0.48
Fe	0.07	0.10	0.03	0.05	-0.02	-0.02	0.05	0.07	0.03	0.02	-0.06	-0.33	0.05	0.07	0.05	0.10
Log Fe	0.15	0.12	-0.03	-0.03	0.00	0.05	0.13	0.10	0.09	0.02	-0.05	-0.44	0.11	0.07	0.12	0.10
U	0.82	0.55	0.08	0.20	0.32	0.33	0.89	0.72	0.83	0.67	0.09	0.16	0.85	0.65	0.75	0.57
Log U	0.61	0.59	-0.02	0.14	0.58	0.59	0.68	0.75	0.76	0.77	0.18	0.27	0.70	0.74	0.56	0.56
Fe-Trec	0.07	0.04	-0.10	-0.07	-0.19	-0.22	-0.02	-0.21	-0.08	-0.18	-0.02	-0.14	0.03	-0.08	-0.16	-0.22
Log Fe-Trec	0.20	0.15	-0.22	-0.15	0.04	0.03	0.15	0.04	0.14	0.08	0.06	-0.01	0.22	0.17	-0.16	-0.22
Lab pH	-0.07	-0.09	-0.03	-0.04	-0.17	-0.15	-0.10	-0.13	-0.14	-0.16	-0.15	-0.09	-0.08	-0.10	-0.05	-0.10
Log Lab pH	-0.07	-0.09	-0.03	-0.04	-0.17	-0.14	-0.10	-0.13	-0.14	-0.15	-0.15	-0.09	-0.08	-0.10	-0.05	-0.10
SAR	0.96	0.88	0.08	0.26	0.35	0.30	0.86	0.78	0.84	0.71	0.25	0.25	0.90	0.74	0.65	0.84
Log SAR	0.80	0.95	0.10	0.30	0.41	0.36	0.72	0.79	0.73	0.73	0.20	0.29	0.81	0.79	0.45	0.86
Adj SAR	0.58	0.71	0.09	0.27	0.35	0.30	0.47	0.56	0.51	0.53	0.23	0.25	0.58	0.59	0.30	0.62
Log Adj SAR	-0.02	0.25	0.06	0.16	0.18	0.16	-0.06	0.14	0.01	0.15	0.11	0.15	0.03	0.19	-0.10	0.15
Lab EC	0.97	0.81	0.07	0.25	0.48	0.40	0.93	0.81	0.79	0.33	0.29	0.90	0.74	0.77	0.80	
Log Lab EC	0.82	0.93	0.10	0.33	0.63	0.58	0.80	0.91	0.89	0.92	0.26	0.34	0.89	0.89	0.51	0.86

APPENDIX F – r_p Values between All Constituents in the Downstream Ground Water (cont.)

	CO3	Log CO3	HCO3	Log	Alk	Log Alk	B	Log B	Cat/An	Log	TDS	Log TDS
Ls	-0.02	-0.02	0.10	0.14	0.07	0.08	0.15	0.16	-0.13	-0.22	0.15	0.11
Log Ls	-0.01	-0.01	0.12	0.14	0.10	0.06	0.07	-0.11	-0.20	0.08	0.05	
WT Depth	-0.02	-0.02	0.01	0.01	0.01	0.01	0.10	0.00	0.02	0.01	0.00	
Log WT Depth	-0.01	-0.03	-0.01	-0.02	0.00	-0.01	0.04	0.17	-0.04	-0.02	0.04	0.03
Field pH	0.04	0.06	-0.12	-0.10	-0.12	-0.09	-0.07	-0.13	0.01	0.00	-0.15	-0.20
Log Field pH	0.04	0.07	-0.12	-0.10	-0.12	-0.09	-0.07	-0.13	0.01	-0.01	-0.15	-0.19
T	-0.01	-0.02	0.07	0.06	0.07	0.06	0.01	0.05	-0.01	-0.01	0.08	0.07
Log T	-0.08	-0.13	0.05	0.04	0.04	0.04	0.05	0.06	-0.04	-0.04	0.04	0.02
Field EC	0.07	-0.01	0.28	0.22	0.28	0.21	0.20	0.52	0.10	0.11	0.89	0.78
Log Field EC	0.01	-0.08	0.35	0.33	0.35	0.31	0.17	0.63	0.06	0.06	0.74	0.85
DO	0.05	0.07	-0.19	-0.19	-0.18	-0.17	0.00	-0.03	-0.05	-0.08	-0.05	-0.11
Log DO	0.04	0.05	-0.17	-0.17	-0.16	-0.16	-0.13	0.03	0.05	-0.08	-0.09	0.00
ORP	0.06	0.08	-0.18	-0.16	-0.17	-0.14	0.00	0.02	-0.05	-0.02	0.02	0.03
Log ORP	0.06	0.08	0.02	0.01	0.04	0.05	-0.01	0.05	-0.05	-0.01	0.03	0.07
Se	0.01	-0.01	-0.10	-0.27	-0.10	-0.26	0.04	0.24	0.05	0.08	0.41	0.32
Log Se	0.02	-0.01	0.14	0.14	0.14	0.13	0.11	0.49	0.01	0.01	0.50	0.51
Fe	No Data	No Data	0.03	0.02	0.04	0.03	0.01	0.03	-0.04	-0.04	0.06	0.07
Log Fe	No Data	No Data	-0.04	-0.06	-0.08	-0.08	0.05	0.00	0.00	0.03	0.13	0.08
U	0.33	0.12	0.26	0.30	0.28	0.31	0.85	0.73	-0.08	-0.08	0.84	0.67
Log U	0.11	-0.02	0.17	0.26	0.17	0.26	0.67	0.74	0.11	0.11	0.68	0.72
Fe-Trec	No Data	No Data	0.03	0.05	0.03	0.05	0.14	0.15	0.00	0.00	0.02	-0.07
Log Fe-Trec	No Data	No Data	-0.10	-0.06	-0.10	-0.06	0.28	0.28	-0.04	-0.05	0.18	0.12
Lab pH	0.23	0.28	-0.08	-0.06	-0.06	-0.03	-0.03	-0.11	-0.03	-0.05	-0.10	-0.13
Log Lab pH	0.21	0.26	-0.07	-0.05	-0.06	-0.03	-0.03	-0.10	-0.03	-0.05	-0.09	-0.12
SAR	0.09	0.01	0.41	0.37	0.41	0.35	0.24	0.61	0.03	0.03	0.94	0.85
Log SAR	0.05	-0.01	0.45	0.44	0.45	0.41	0.18	0.65	-0.01	-0.01	0.80	0.87
Adj SAR	-0.07	-0.07	0.32	0.31	0.31	0.29	0.21	0.50	0.01	0.01	0.57	0.66
Log Adj SAR	-0.16	-0.09	0.07	0.10	0.06	0.08	0.06	0.17	-0.01	-0.01	0.00	0.20
Lab EC	0.09	0.01	0.35	0.29	0.35	0.28	0.20	0.59	0.09	0.10	0.97	0.85
Log Lab EC	0.04	-0.03	0.43	0.41	0.43	0.38	0.19	0.73	0.06	0.07	0.88	0.97

APPENDIX F – r_p Values between All Constituents in the Downstream Ground Water (cont.)

	Ls	Log Ls	WT Depth	Log WT Depth	Field pH	Log Field pH	T	Log T	Field EC	Log	DO	Log DO	ORP	Log ORP
Na	0.24	0.16	0.01	0.02	-0.11	-0.11	0.07	0.03	0.89	0.69	-0.03	0.02	0.00	0.00
Log Na	0.22	0.15	-0.01	0.00	-0.15	-0.15	0.07	0.02	0.76	0.82	-0.08	-0.02	0.01	0.05
K	-0.13	-0.07	-0.02	0.01	-0.09	-0.08	0.04	0.04	0.09	0.12	-0.11	-0.09	-0.11	0.08
Log K	-0.23	-0.17	0.00	0.08	-0.12	-0.11	0.07	0.05	0.24	0.32	-0.14	-0.05	-0.06	0.11
Ca	-0.19	-0.23	0.05	0.09	-0.23	-0.23	0.04	-0.01	0.45	0.61	-0.17	-0.12	0.03	0.10
Log Ca	-0.17	-0.21	0.03	0.05	-0.19	-0.19	0.03	-0.03	0.36	0.51	-0.15	-0.11	0.02	0.08
Mg	0.21	0.14	-0.01	0.03	-0.11	-0.12	0.08	0.06	0.85	0.67	-0.02	0.02	0.02	0.01
Log Mg	0.21	0.14	-0.06	-0.02	-0.14	-0.14	0.08	0.05	0.75	0.80	-0.09	-0.04	0.04	0.05
Hard	0.05	-0.01	0.01	0.06	-0.16	-0.16	0.08	0.04	0.86	0.76	-0.07	-0.02	0.03	0.05
Log Hard	0.03	-0.03	0.00	0.05	-0.19	-0.19	0.07	0.02	0.73	0.81	-0.13	-0.06	0.04	0.08
NO3	0.08	0.07	-0.01	0.02	-0.18	-0.20	0.00	-0.03	0.38	0.25	0.01	0.03	0.08	0.07
Log NO3	0.07	0.02	0.06	0.11	-0.17	-0.17	0.01	-0.02	0.29	0.30	0.16	0.20	0.21	0.15
SO4	0.14	0.06	0.02	0.07	-0.14	-0.14	0.08	0.05	0.80	0.74	-0.04	0.02	0.03	0.04
Log SO4	0.10	0.03	0.00	0.04	-0.17	-0.17	0.06	0.02	0.68	0.78	-0.08	-0.01	0.07	0.08
Cl	0.09	0.03	0.00	-0.03	-0.07	-0.07	0.06	0.01	0.76	0.44	0.00	0.00	0.01	0.01
Log Cl	0.10	0.05	0.01	0.00	-0.16	-0.16	0.10	0.04	0.75	0.75	-0.12	-0.10	0.03	0.09
CO3	-0.02	-0.01	-0.02	-0.01	0.04	0.04	-0.01	-0.08	0.07	0.01	0.05	0.04	0.06	0.06
Log CO3	-0.02	-0.01	-0.02	-0.03	0.06	0.07	-0.02	-0.13	-0.01	-0.08	0.07	0.05	0.08	0.08
HCO3	0.10	0.12	0.01	-0.01	-0.12	-0.12	0.07	0.05	0.28	0.35	-0.19	-0.17	-0.18	0.02
Log HCO3	0.14	0.14	0.01	-0.02	-0.10	-0.10	0.06	0.04	0.22	0.33	-0.19	-0.17	-0.16	0.01
Alk	0.07	0.10	0.01	0.00	-0.12	-0.12	0.07	0.04	0.28	0.35	-0.18	-0.16	-0.17	0.04
Log Alk	0.08	0.10	0.01	-0.01	-0.09	-0.09	0.06	0.04	0.21	0.31	-0.17	-0.13	-0.14	0.05
B	0.15	0.06	0.01	0.04	-0.07	-0.07	0.01	0.05	0.20	0.17	0.00	0.03	0.00	-0.01
Log B	0.16	0.07	0.10	0.17	-0.13	-0.13	0.05	0.06	0.52	0.63	-0.03	0.05	0.02	0.05
Cat/An	-0.13	-0.11	0.00	-0.04	0.01	0.01	-0.01	-0.04	0.10	0.06	-0.05	-0.08	-0.05	-0.05
Log Cat/An	-0.22	-0.20	0.02	-0.02	0.00	-0.01	-0.01	-0.04	0.11	0.06	-0.08	-0.09	-0.02	-0.01
TDS	0.15	0.08	0.01	0.04	-0.15	-0.15	0.08	0.04	0.89	0.74	-0.05	0.00	0.02	0.03
Log TDS	0.11	0.05	0.00	0.03	-0.20	-0.19	0.07	0.02	0.78	0.85	-0.11	-0.05	0.03	0.07

APPENDIX F – r_p Values between All Constituents in the Downstream Ground Water (cont.)

	Se	Log Se	Fe	Log Fe	U	Log U	Fe-Trec	Log Fe-Trec	Lab pH	Log Lab	SAR	Log SAR	Adj SAR	Log Adj SAR	Lab EC	Log Lab EC
Na	0.38	0.47	0.07	0.15	0.82	0.61	0.07	0.20	-0.07	-0.07	0.96	0.80	0.58	-0.02	0.97	0.82
Log Na	0.29	0.50	0.10	0.12	0.55	0.59	0.04	0.15	-0.09	-0.09	0.88	0.95	0.71	0.25	0.81	0.93
K	-0.01	-0.03	0.03	-0.03	0.08	-0.02	-0.10	-0.22	-0.03	-0.03	0.08	0.10	0.09	0.06	0.07	0.10
Log K	0.03	0.11	0.05	-0.03	0.20	0.14	-0.07	-0.15	-0.04	-0.04	0.26	0.30	0.27	0.16	0.25	0.33
Ca	0.16	0.31	-0.02	0.00	0.32	0.58	-0.19	0.04	-0.17	-0.17	0.35	0.41	0.35	0.18	0.48	0.68
Log Ca	0.11	0.24	-0.02	0.05	0.33	0.59	-0.22	0.03	-0.15	-0.14	0.30	0.36	0.30	0.16	0.40	0.58
Mg	0.43	0.47	0.05	0.13	0.89	0.68	-0.02	0.15	-0.10	-0.10	0.86	0.72	0.47	-0.06	0.93	0.80
Log Mg	0.32	0.49	0.07	0.10	0.72	0.75	-0.21	0.04	-0.13	-0.13	0.78	0.79	0.56	0.14	0.81	0.91
Hard	0.41	0.50	0.03	0.09	0.83	0.76	-0.08	0.14	-0.14	-0.14	0.84	0.73	0.51	0.01	0.93	0.89
Log Hard	0.30	0.47	0.02	0.02	0.67	0.77	-0.18	0.08	-0.16	-0.15	0.71	0.73	0.53	0.15	0.79	0.92
NO ₃	0.97	0.31	-0.06	-0.05	0.09	0.18	-0.02	0.06	-0.15	-0.15	0.25	0.20	0.23	0.11	0.33	0.26
Log NO ₃	0.35	0.69	-0.33	-0.44	0.16	0.27	-0.14	-0.01	-0.09	-0.09	0.25	0.29	0.25	0.15	0.29	0.34
SO ₄	0.30	0.50	0.05	0.11	0.85	0.70	0.03	0.22	-0.08	-0.08	0.90	0.81	0.58	0.03	0.90	0.89
Log SO ₄	0.23	0.46	0.07	0.07	0.65	0.74	-0.08	0.17	-0.10	-0.10	0.74	0.79	0.59	0.19	0.74	0.89
Cl	0.38	0.29	0.05	0.12	0.75	0.56	-0.16	-0.16	-0.05	-0.05	0.65	0.45	0.30	-0.10	0.77	0.51
Log Cl	0.32	0.48	0.10	0.10	0.57	0.56	-0.22	-0.22	-0.10	-0.10	0.84	0.86	0.62	0.15	0.80	0.86
CO ₃	0.01	0.02	No Data	No Data	0.33	0.11	No Data	No Data	0.23	0.21	0.09	0.05	-0.07	-0.16	0.09	0.04
Log CO ₃	-0.01	-0.01	No Data	No Data	0.12	-0.02	No Data	No Data	0.28	0.26	0.01	-0.01	-0.07	-0.09	0.01	-0.03
HCO ₃	-0.10	0.14	0.03	-0.04	0.26	0.17	0.03	-0.10	-0.08	-0.07	0.41	0.45	0.32	0.07	0.35	0.43
Log HCO ₃	-0.27	0.14	0.02	-0.06	0.30	0.26	0.05	-0.06	-0.05	-0.05	0.37	0.44	0.31	0.10	0.29	0.41
Alk	-0.10	0.14	0.04	-0.08	0.28	0.17	0.03	-0.10	-0.06	-0.06	0.41	0.45	0.31	0.06	0.35	0.43
Log Alk	-0.26	0.13	0.03	-0.08	0.31	0.26	0.05	-0.06	-0.03	-0.03	0.35	0.41	0.29	0.08	0.28	0.38
B	0.04	0.11	0.01	0.05	0.85	0.67	0.14	0.28	-0.03	-0.03	0.24	0.18	0.21	0.06	0.20	0.19
Log B	0.24	0.49	0.03	0.00	0.73	0.74	0.15	0.28	-0.11	-0.10	0.61	0.65	0.50	0.17	0.59	0.73
Cat/An	0.05	0.01	-0.04	0.00	-0.08	0.11	0.00	-0.04	-0.03	-0.03	0.03	-0.01	0.01	-0.01	0.09	0.06
Log Cat/An	0.08	0.01	-0.04	0.03	-0.08	0.11	0.00	-0.05	-0.05	-0.05	0.03	-0.01	0.01	-0.01	0.10	0.07
TDS	0.41	0.50	0.06	0.13	0.84	0.68	0.02	0.18	-0.10	-0.09	0.94	0.80	0.57	0.00	0.97	0.88
Log TDS	0.32	0.51	0.07	0.08	0.67	0.72	-0.07	0.12	-0.13	-0.12	0.85	0.87	0.66	0.20	0.85	0.97

APPENDIX F – r_p Values between All Constituents in the Downstream Ground Water (cont.)

	Na	Log Na	K	Log K	Ca	Log Ca	Mg	Log Mg	Hard	Log	NO3	Log NO3	SO4	Log SO4	Cl	Log Cl
Na	1.00	0.80	0.07	0.23	0.37	0.31	0.93	0.77	0.90	0.72	0.29	0.24	0.91	0.70	0.78	0.79
Log Na	0.80	1.00	0.08	0.31	0.56	0.49	0.76	0.88	0.81	0.84	0.21	0.31	0.85	0.86	0.46	0.86
K	0.07	0.08	1.00	0.76	0.01	0.02	0.04	0.03	0.04	0.04	0.01	0.12	0.04	0.00	0.05	0.20
Log K	0.23	0.31	0.76	1.00	0.26	0.24	0.21	0.25	0.27	0.30	0.03	0.16	0.28	0.27	0.10	0.37
Ca	0.37	0.56	0.01	0.26	1.00	0.88	0.41	0.64	0.65	0.82	0.14	0.29	0.52	0.68	0.26	0.53
Log Ca	0.31	0.49	0.02	0.24	0.88	1.00	0.34	0.55	0.53	0.70	0.10	0.24	0.44	0.59	0.18	0.44
Mg	0.93	0.76	0.04	0.21	0.41	0.34	1.00	0.85	0.94	0.77	0.32	0.25	0.91	0.71	0.72	0.74
Log Mg	0.77	0.88	0.03	0.25	0.64	0.55	0.85	1.00	0.90	0.94	0.23	0.32	0.88	0.88	0.46	0.78
Hard	0.90	0.81	0.04	0.27	0.65	0.53	0.94	0.90	1.00	0.91	0.31	0.31	0.93	0.81	0.69	0.79
Log Hard	0.72	0.84	0.04	0.30	0.82	0.70	0.77	0.94	0.91	1.00	0.22	0.34	0.85	0.90	0.44	0.77
NO3	0.29	0.21	0.01	0.03	0.14	0.10	0.32	0.23	0.31	0.22	1.00	0.38	0.20	0.16	0.29	0.22
Log NO3	0.24	0.31	0.12	0.16	0.29	0.24	0.25	0.32	0.31	0.34	0.38	1.00	0.24	0.29	0.23	0.35
SO4	0.91	0.85	0.04	0.28	0.52	0.44	0.91	0.88	0.93	0.85	0.20	0.24	1.00	0.87	0.54	0.79
Log SO4	0.70	0.86	0.00	0.27	0.68	0.59	0.71	0.88	0.81	0.90	0.16	0.29	0.87	1.00	0.37	0.75
Cl	0.78	0.46	0.05	0.10	0.26	0.18	0.72	0.46	0.69	0.44	0.29	0.23	0.54	0.37	1.00	0.60
Log Cl	0.79	0.86	0.20	0.37	0.53	0.44	0.74	0.78	0.79	0.77	0.22	0.35	0.79	0.75	0.60	1.00
CO3	0.10	0.04	-0.01	0.00	-0.05	-0.04	0.10	0.03	0.07	0.02	-0.01	-0.04	0.09	0.03	0.04	0.05
Log CO3	0.02	-0.02	-0.03	-0.04	-0.08	-0.07	0.01	-0.04	-0.02	-0.06	-0.02	-0.05	0.00	-0.04	0.00	-0.01
HCO3	0.35	0.44	0.45	0.42	0.25	0.21	0.31	0.37	0.34	0.37	-0.13	0.05	0.38	0.33	0.13	0.45
Log HCO3	0.30	0.43	0.35	0.37	0.28	0.23	0.25	0.36	0.30	0.36	-0.30	0.06	0.35	0.34	0.09	0.43
Alk	0.35	0.44	0.45	0.43	0.24	0.20	0.31	0.37	0.33	0.36	-0.13	0.05	0.38	0.33	0.13	0.45
Log Alk	0.29	0.41	0.34	0.38	0.25	0.21	0.24	0.33	0.28	0.34	-0.30	0.06	0.34	0.34	0.09	0.41
B	0.24	0.19	0.02	0.08	0.06	0.05	0.24	0.19	0.22	0.18	0.02	0.01	0.26	0.18	0.08	0.17
Log B	0.55	0.69	0.03	0.21	0.47	0.40	0.61	0.74	0.66	0.71	0.15	0.22	0.74	0.70	0.13	0.55
Cat/An	0.07	0.03	0.01	0.02	0.20	0.21	0.05	0.02	0.09	0.09	0.06	0.04	-0.08	-0.28	0.18	0.07
Log Cat/An	0.08	0.03	0.02	0.04	0.31	0.37	0.05	0.01	0.11	0.10	0.08	0.07	-0.09	-0.21	0.22	0.11
TDS	0.98	0.83	0.08	0.27	0.50	0.41	0.95	0.84	0.96	0.82	0.31	0.28	0.95	0.79	0.75	0.82
Log TDS	0.81	0.94	0.10	0.35	0.71	0.62	0.81	0.94	0.90	0.95	0.24	0.34	0.92	0.95	0.49	0.86

APPENDIX F – r_p Values between All Constituents in the Downstream Ground Water (cont.)

	CO3	Log CO3	HCO3	Log	Alk	Log Alk	B	Log B	Cat/An	Log	TDS	Log TDS
Na	0.10	0.02	0.35	0.30	0.35	0.29	0.24	0.55	0.07	0.08	0.98	0.81
Log Na	0.04	-0.02	0.44	0.43	0.44	0.41	0.19	0.69	0.03	0.03	0.83	0.94
K	-0.01	-0.03	0.45	0.35	0.45	0.34	0.02	0.03	0.01	0.02	0.08	0.10
Log K	0.00	-0.04	0.42	0.37	0.43	0.38	0.08	0.21	0.02	0.04	0.27	0.35
Ca	-0.05	-0.08	0.25	0.28	0.24	0.25	0.06	0.47	0.20	0.31	0.50	0.71
Log Ca	-0.04	-0.07	0.21	0.23	0.20	0.21	0.05	0.40	0.21	0.37	0.41	0.62
Mg	0.10	0.01	0.31	0.25	0.31	0.24	0.24	0.61	0.05	0.05	0.95	0.81
Log Mg	0.03	-0.04	0.37	0.36	0.37	0.33	0.19	0.74	0.02	0.01	0.84	0.94
Hard	0.07	-0.02	0.34	0.30	0.33	0.28	0.22	0.66	0.09	0.11	0.96	0.90
Log Hard	0.02	-0.06	0.37	0.36	0.36	0.34	0.18	0.71	0.09	0.10	0.82	0.95
NO3	-0.01	-0.02	-0.13	-0.30	-0.13	-0.30	0.02	0.15	0.06	0.08	0.31	0.24
Log NO3	-0.04	-0.05	0.05	0.06	0.05	0.06	0.01	0.22	0.04	0.07	0.28	0.34
SO4	0.09	0.00	0.38	0.35	0.38	0.34	0.26	0.74	-0.08	-0.09	0.95	0.92
Log SO4	0.03	-0.04	0.33	0.34	0.33	0.34	0.18	0.70	-0.28	-0.21	0.79	0.95
Cl	0.04	0.00	0.13	0.09	0.13	0.09	0.08	0.13	0.18	0.22	0.75	0.49
Log Cl	0.05	-0.01	0.45	0.43	0.45	0.41	0.17	0.55	0.07	0.11	0.82	0.86
CO3	1.00	0.86	0.00	0.00	0.04	0.04	0.00	0.00	-0.01	-0.02	0.08	0.03
Log CO3	0.86	1.00	-0.05	-0.05	-0.01	-0.01	-0.01	-0.07	-0.02	-0.03	0.00	-0.04
HCO3	0.00	-0.05	1.00	0.94	0.99	0.89	0.12	0.38	-0.09	-0.16	0.38	0.46
Log HCO3	0.00	-0.05	0.94	1.00	0.93	0.95	0.11	0.37	-0.09	-0.16	0.33	0.44
Alk	0.04	-0.01	0.99	0.93	1.00	0.93	0.12	0.37	-0.13	-0.18	0.38	0.45
Log Alk	0.04	-0.01	0.89	0.95	0.93	1.00	0.10	0.35	-0.19	-0.23	0.32	0.43
B	0.00	-0.01	0.12	0.11	0.12	0.10	1.00	0.41	-0.02	-0.02	0.23	0.19
Log B	0.00	-0.07	0.38	0.37	0.37	0.35	0.41	1.00	-0.08	-0.14	0.62	0.74
Cat/An	-0.01	-0.02	-0.09	-0.09	-0.13	-0.19	-0.02	-0.08	1.00	0.92	0.02	-0.05
Log Cat/An	-0.02	-0.03	-0.16	-0.16	-0.18	-0.23	-0.02	-0.14	0.92	1.00	0.03	-0.02
TDS	0.08	0.00	0.38	0.33	0.38	0.32	0.23	0.62	0.02	0.03	1.00	0.88
Log TDS	0.03	-0.04	0.46	0.44	0.45	0.43	0.19	0.74	-0.05	-0.02	0.88	1.00

APPENDIX G – Additional Contour Plots

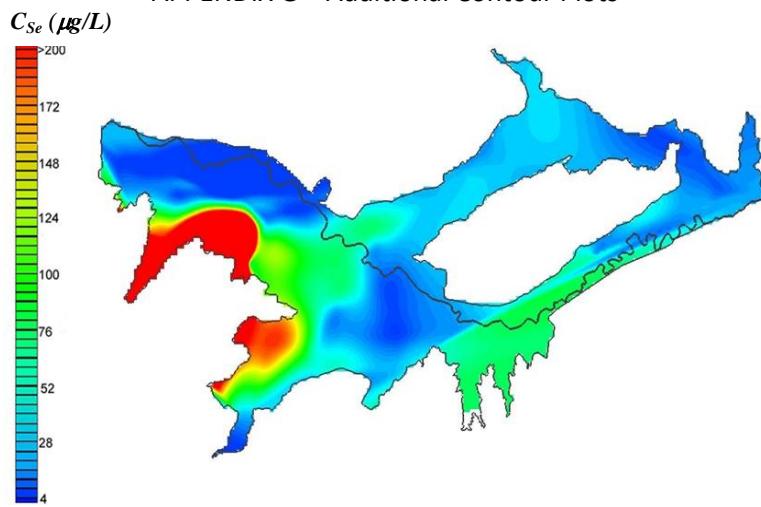


Figure G.1. Contour plot of C_{Se} from samples collected during June 17-20, 2006 in the Upstream Study Region.

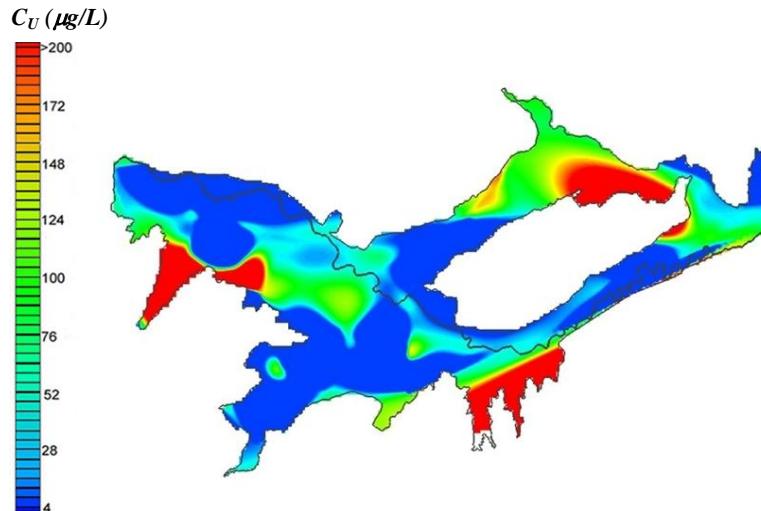


Figure G.2. Contour plot of C_U from samples collected during June 17-20, 2006 in the Upstream Study Region.

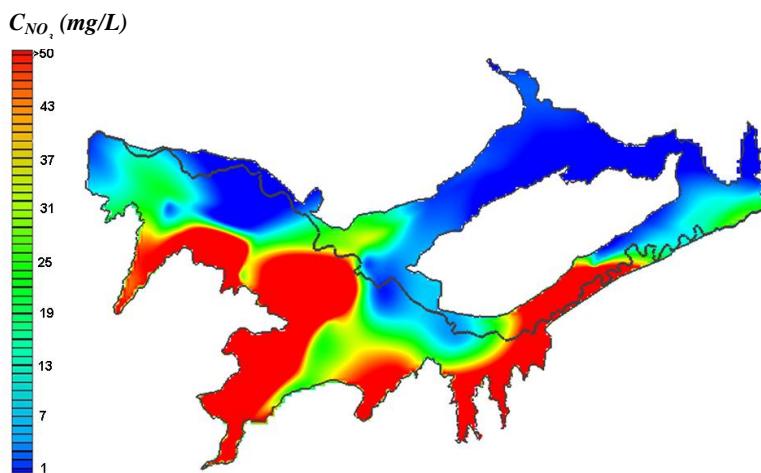


Figure G.3. Contour plot of C_{NO_3} from samples collected during June 17-20, 2006 in the Upstream Study Region.

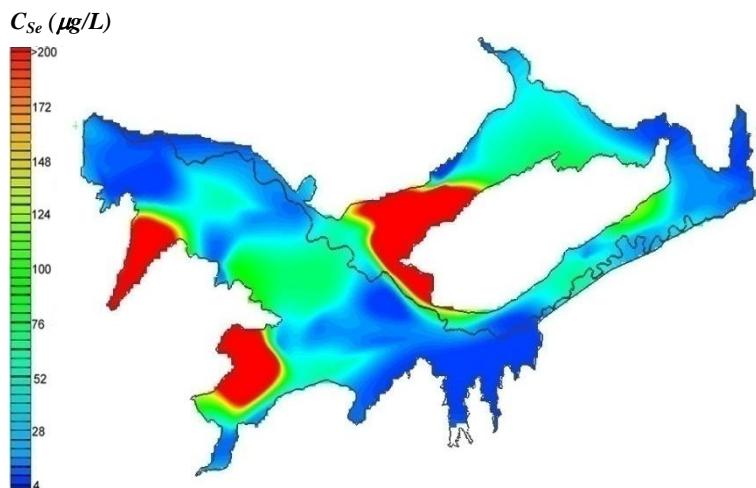


Figure G.4. Contour plot of C_{Se} from samples collected during May 21-24, 2007 in the Upstream Study Region.

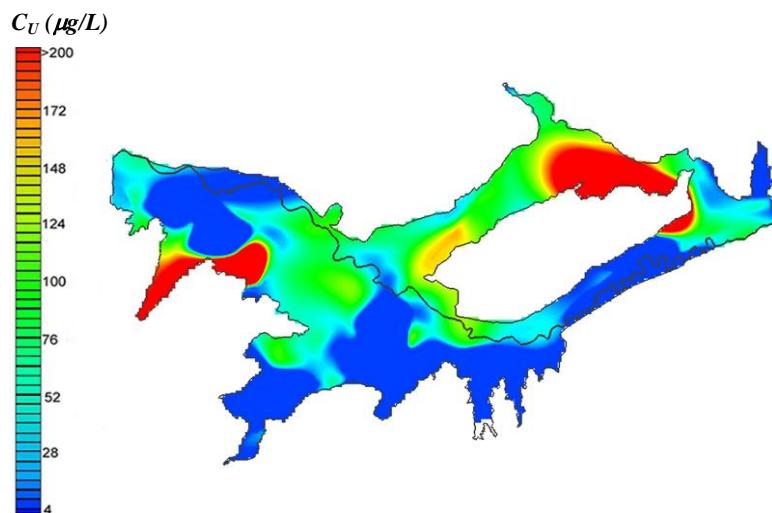


Figure G.5. Contour plot of C_U from samples collected during May 21-24, 2007 in the Upstream Study Region.

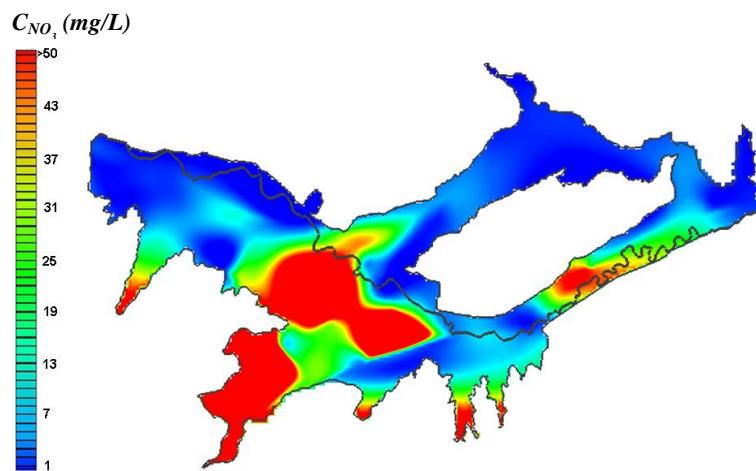


Figure G.6. Contour plot of C_{NO_3} from samples collected during May 21-24, 2007 in the Upstream Study Region.

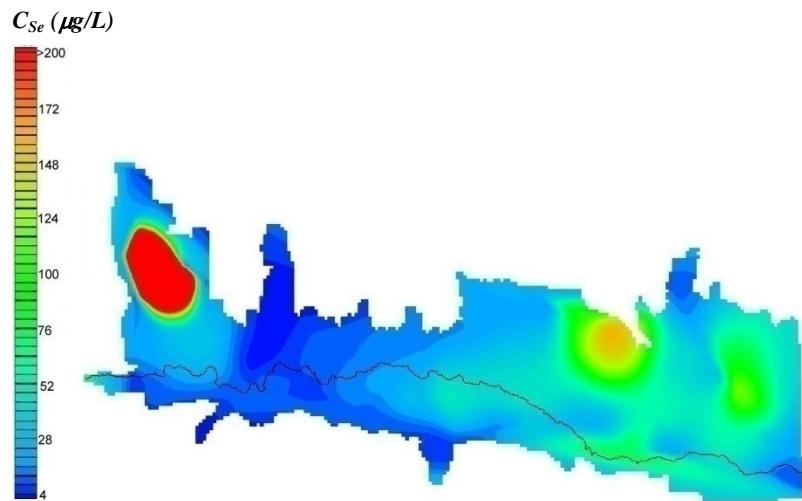


Figure G.7. Contour plot of C_{Se} from samples collected during April 25 - May 5, 2003 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

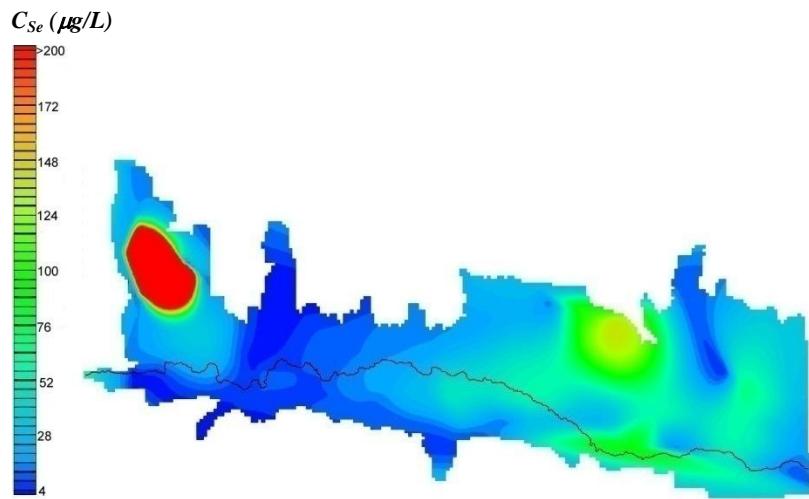


Figure G.8. Contour plot of C_{Se} from samples collected during May 29 - June 11, 2003 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

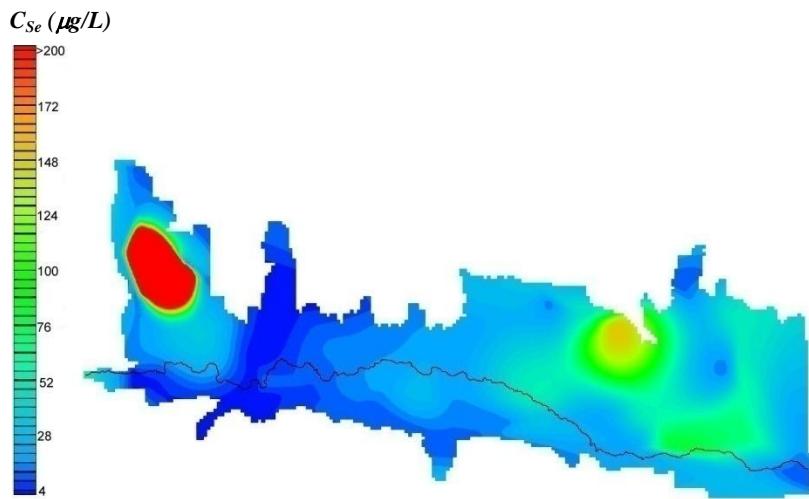


Figure G.9. Contour plot of C_{Se} from samples collected during June 30 - July 8, 2003 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

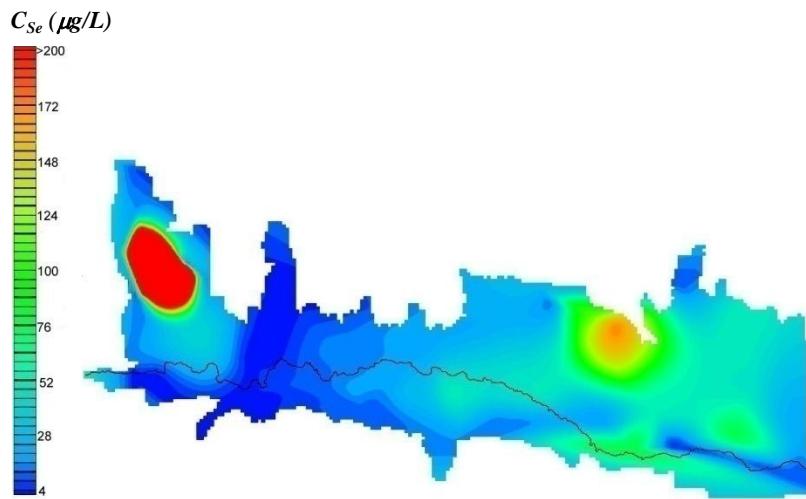


Figure G.10. Contour plot of C_{Se} from samples collected during July 27 – 31, 2003 in the Downstream Study Region.

No C_U Data
During this Event

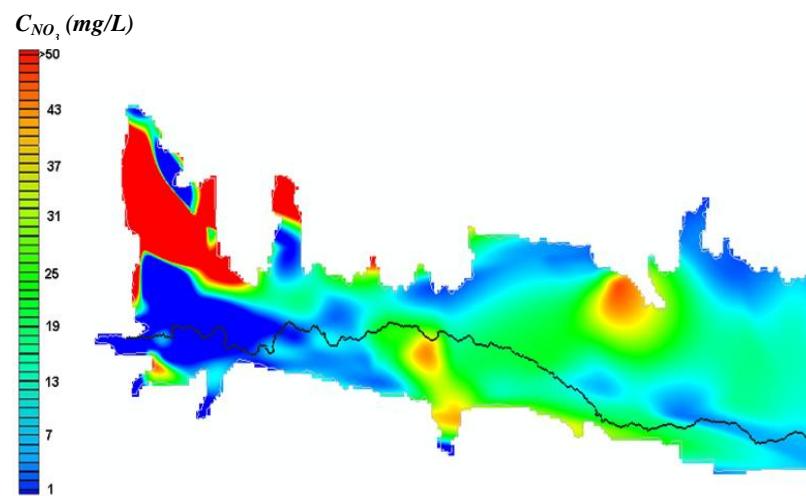


Figure G.11. Contour plot of C_{NO_3} from samples collected during July 27 – 31, 2003 in the Downstream Study Region.

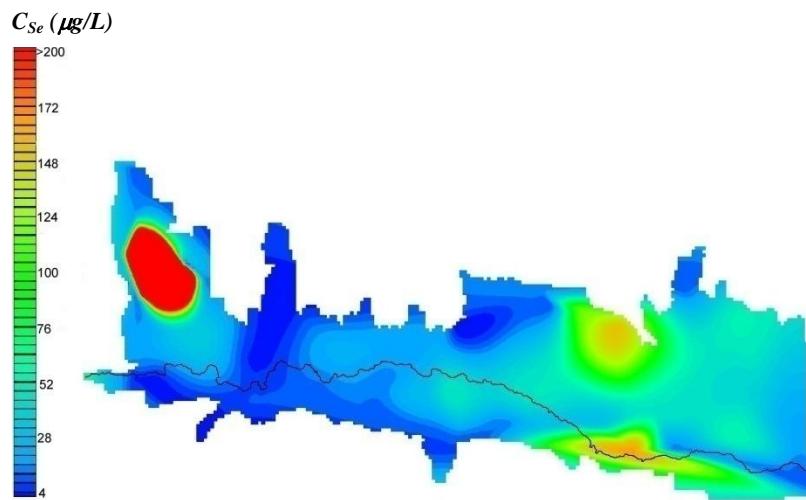


Figure G.12. Contour plot of C_{Se} from samples collected during October 25 - November 2, 2003 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

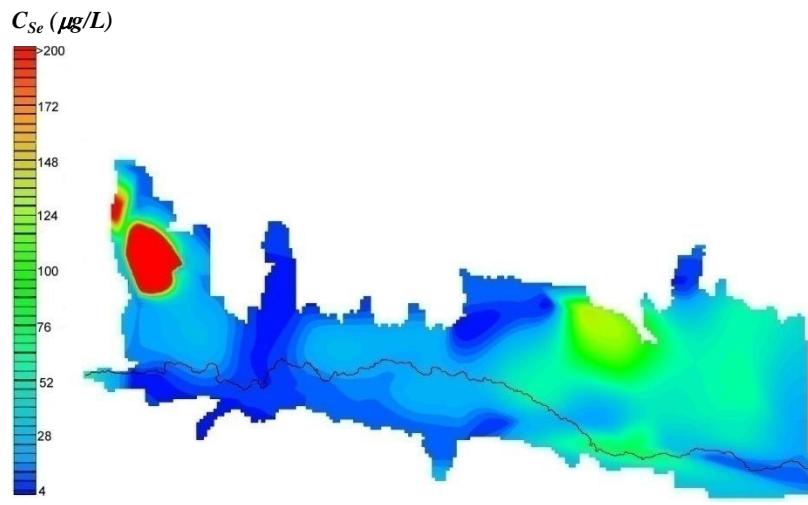


Figure G.13. Contour plot of C_{Se} from samples collected during January 12 – 16, 2004 in the Downstream Study Region.

No C_U Data
During this Event

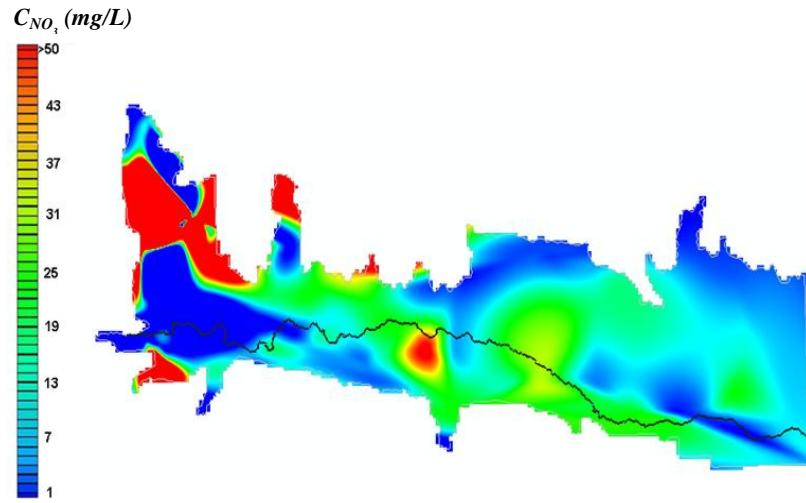


Figure G.14. Contour plot of C_{NO_3} from samples collected during January 12 – 16, 2004 in the Downstream Study Region.

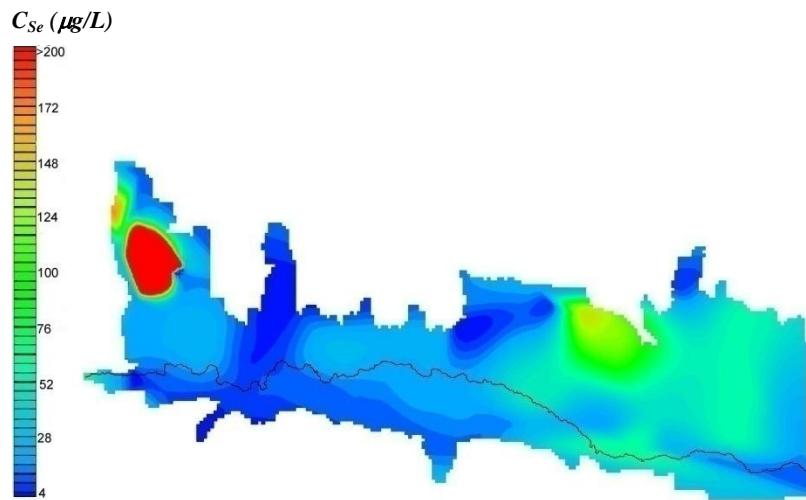


Figure G.15. Contour plot of C_{Se} from samples collected during March 15 – 18, 2004 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

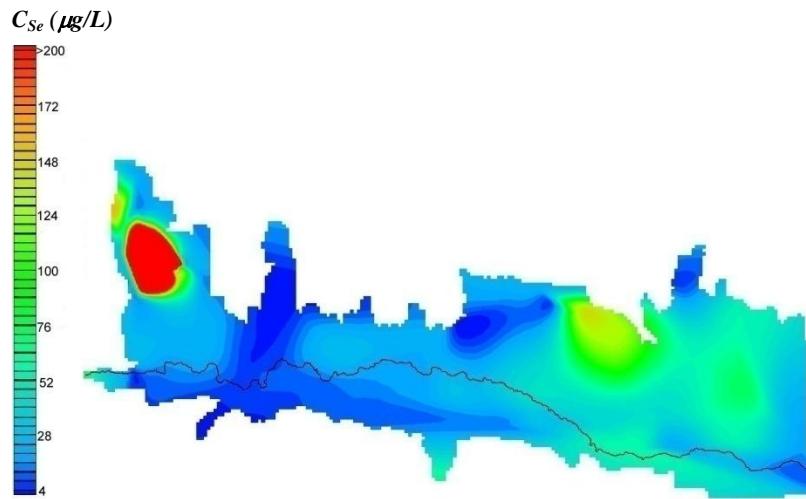


Figure G.16. Contour plot of C_{Se} from samples collected during April 30 - May 3, 2004 in the Downstream Study Region.

No C_U Data
During this Event

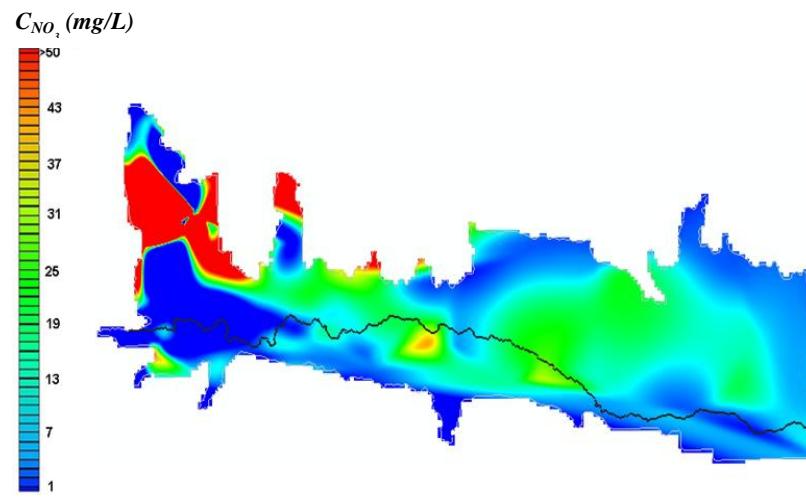


Figure G.17. Contour plot of C_{NO_3} from samples collected during April 30 - May 3, 2004 in the Downstream Study Region.

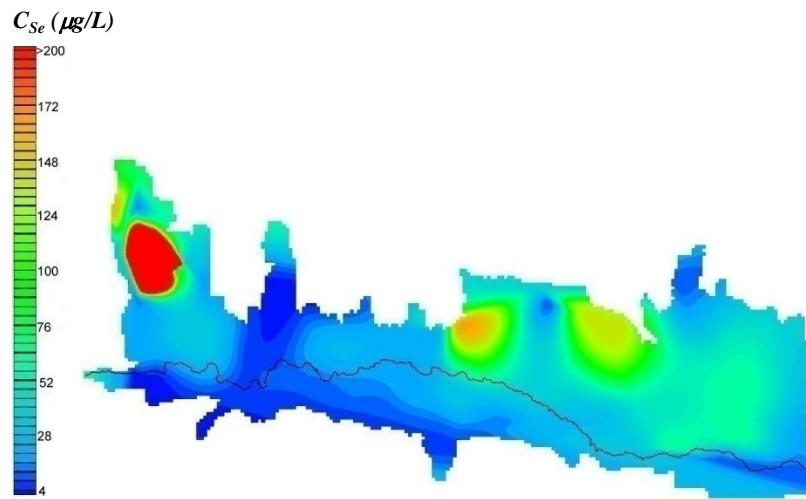


Figure G.18. Contour plot of C_{Se} from samples collected during June 1 – 4, 2004 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

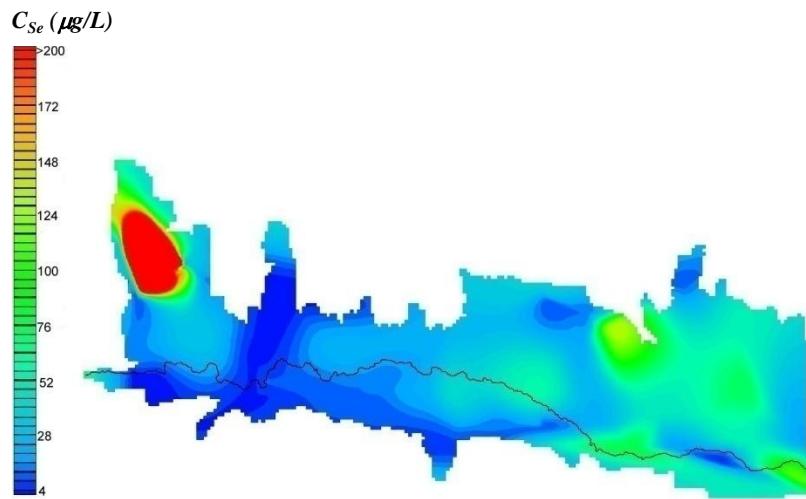


Figure G.19. Contour plot of C_{Se} from samples collected during June 28 – July 1, 2004 in the Downstream Study Region.

No C_U Data
During this Event

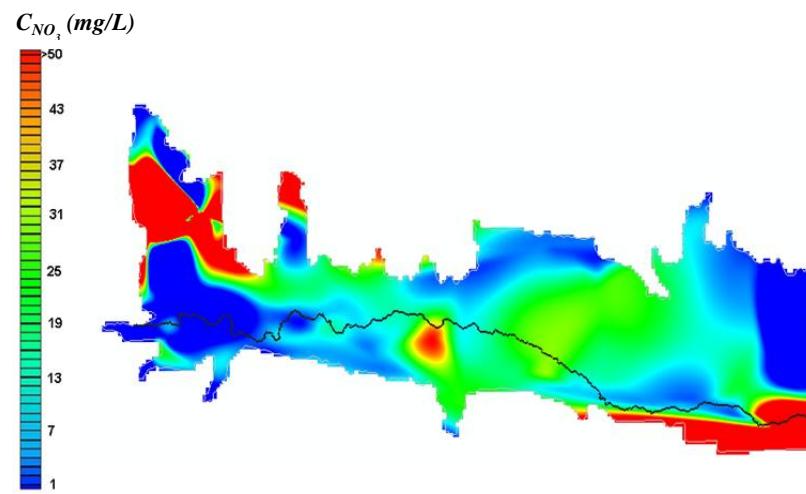


Figure G.20. Contour plot of C_{NO_3} from samples collected during June 28 – July 1, 2004 in the Downstream Study Region.

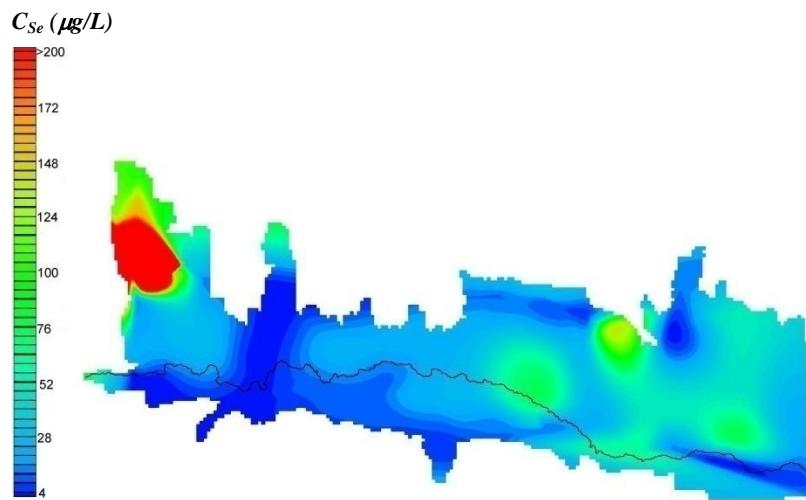


Figure G.21. Contour plot of C_{Se} from samples collected during August 2 – 5, 2004 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

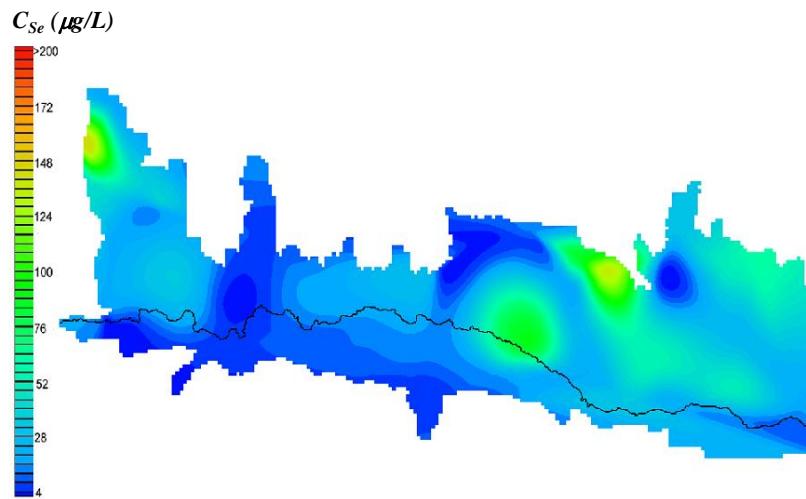


Figure G.22. Contour plot of C_{Se} from samples collected during November 4 -8, 2004 in the Downstream Study Region.

No C_U Data
During this Event

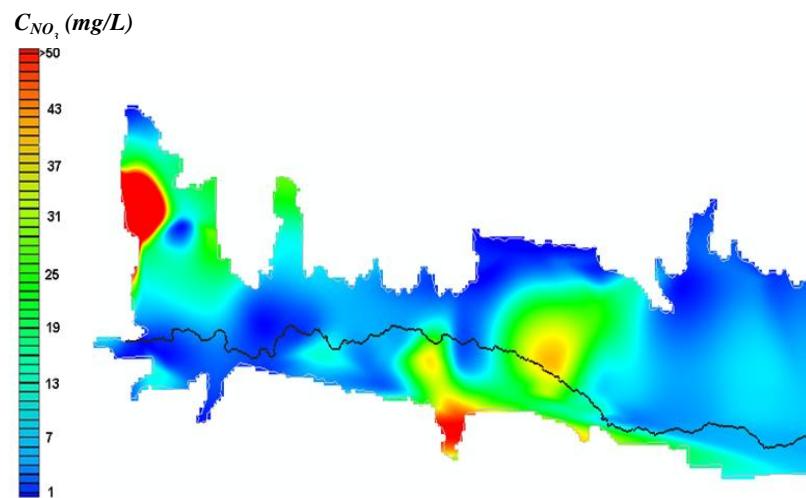


Figure G.23. Contour plot of C_{NO_3} from samples collected during November 4 -8, 2004 in the Downstream Study Region.

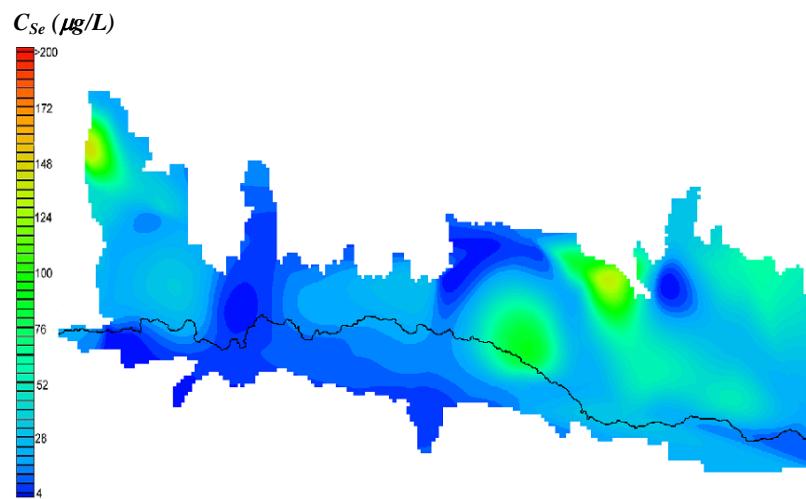


Figure G.24. Contour plot of C_{Se} from samples collected during January 10-14, 2005 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

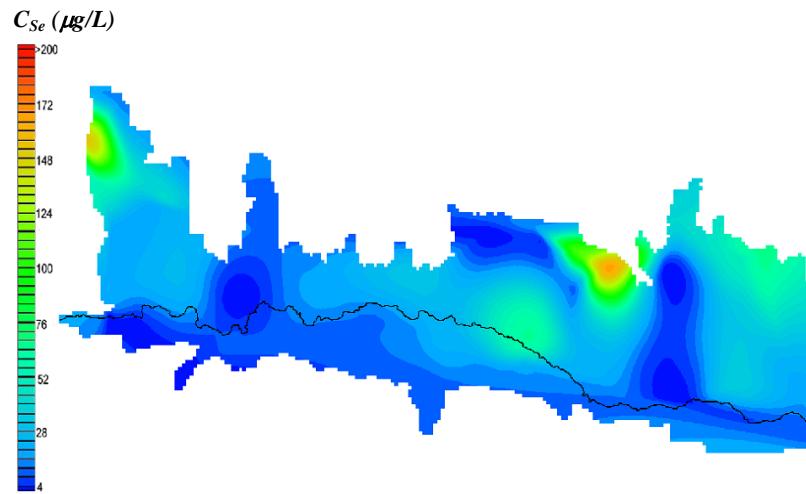


Figure G.25. Contour plot of C_{Se} from samples collected during March 14 – 20, 2005 in the Downstream Study Region.

No C_U Data
During this Event

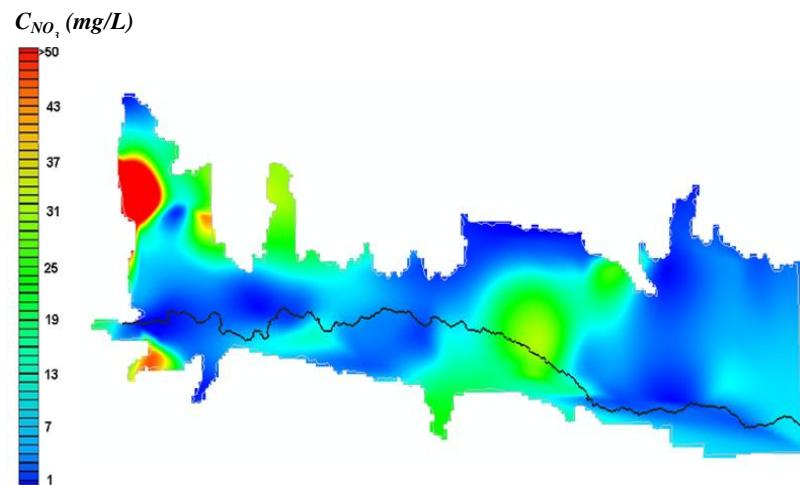


Figure G.26. Contour plot of C_{NO_3} from samples collected during March 14 – 20, 2005 in the Downstream Study Region.

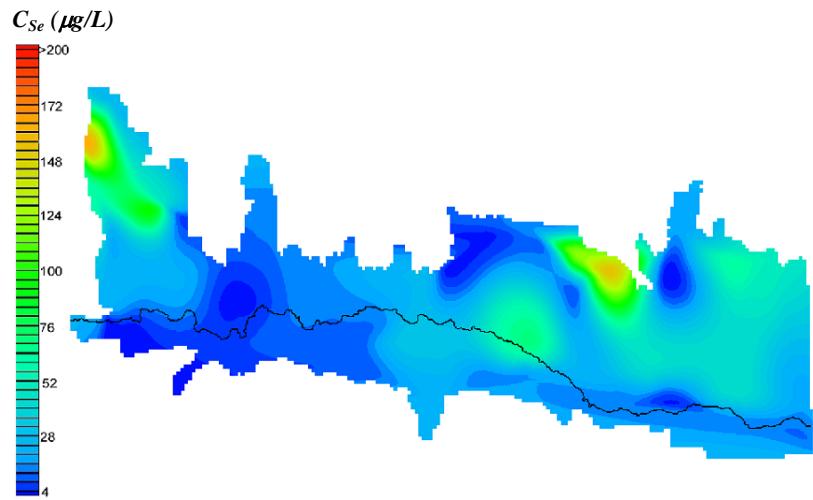


Figure G.27. Contour plot of C_{Se} from samples collected during June 27 to July 2, 2005 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

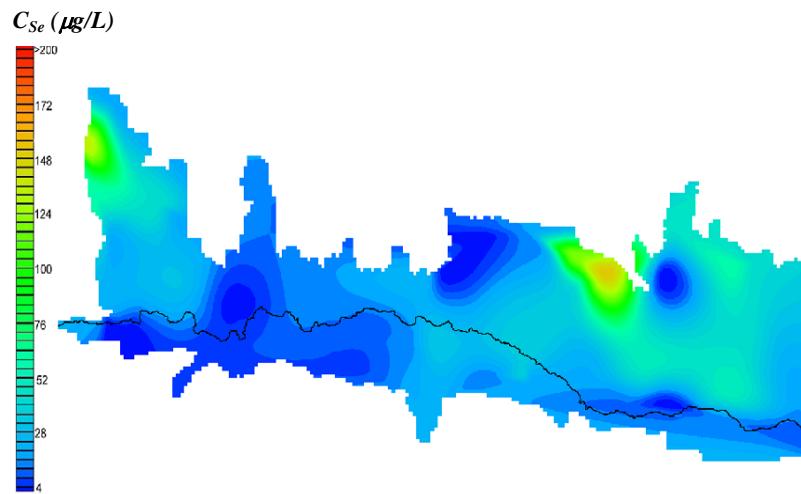


Figure G.28. Contour plot of C_{Se} from samples collected during July 18 – 23, 2005 in the Downstream Study Region.

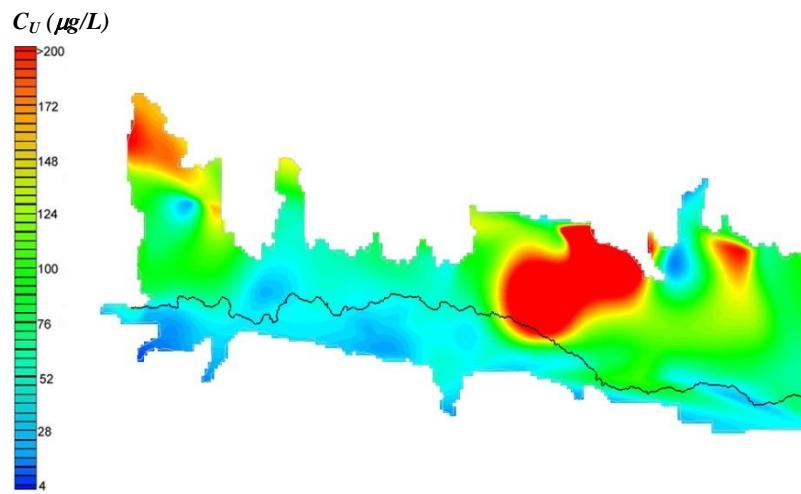


Figure G.29. Contour plot of C_U from samples collected during July 18 – 23, 2005 in the Downstream Study Region.

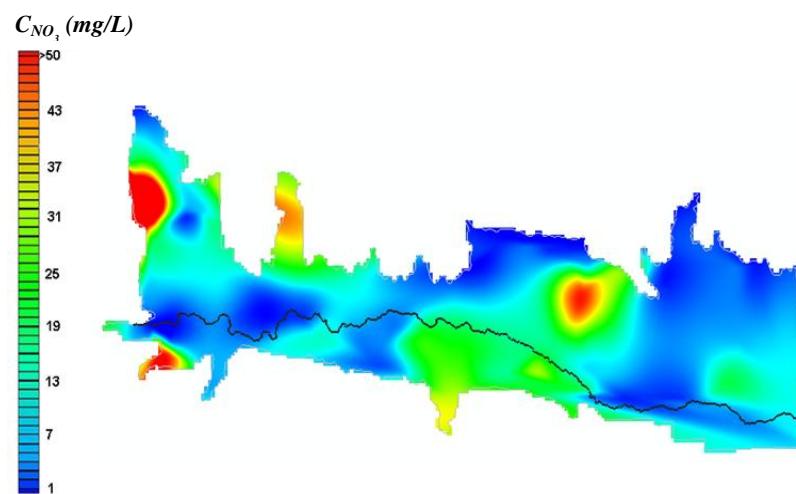


Figure G.30. Contour plot of C_{NO_3} from samples collected during July 18 – 23, 2005 in the Downstream Study Region.

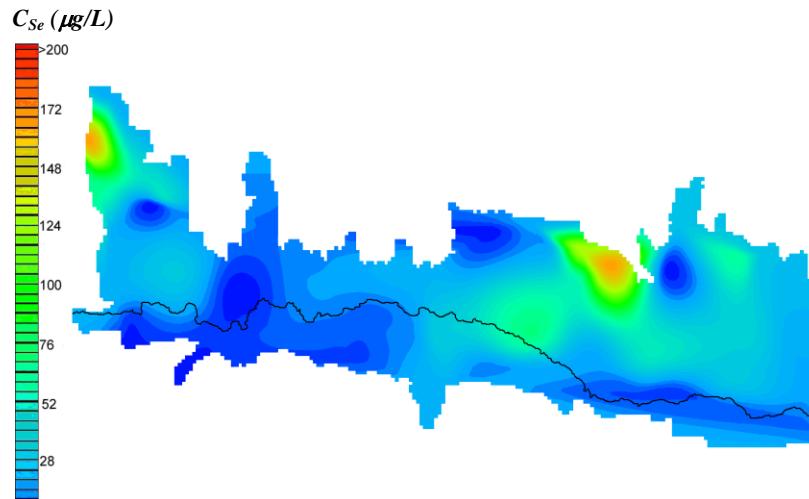


Figure G.31. Contour plot of C_{Se} from samples collected during August 15-22, 2005 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

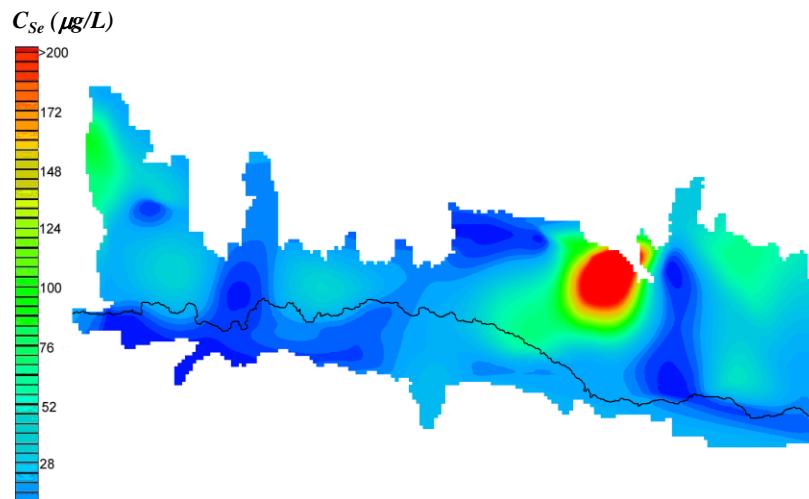


Figure G.32. Contour plot of C_{Se} from samples collected during November 19 – 22 and December 3, 2005 in the Downstream Study Region.

No C_U Data
During this Event

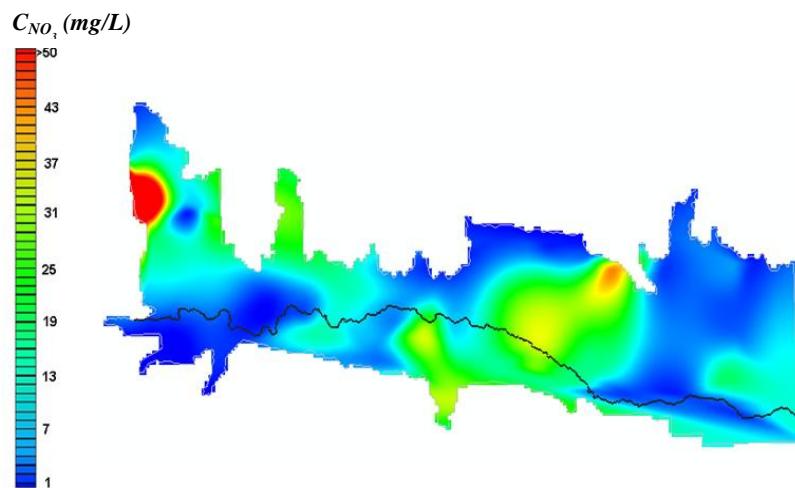


Figure G.33. Contour plot of C_{NO_3} from samples collected during November 19 – 22 and December 3, 2005 in the Downstream Study Region.

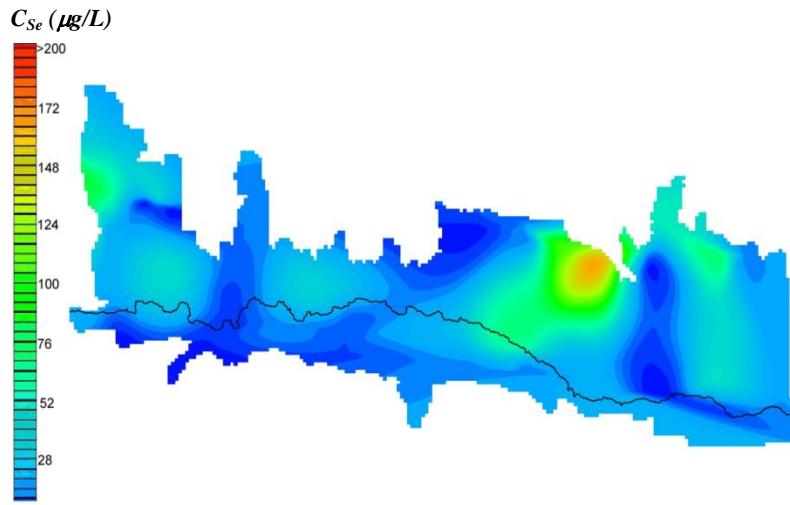


Figure G.34. Contour plot of C_{Se} from samples collected during January 10-14, 2006 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

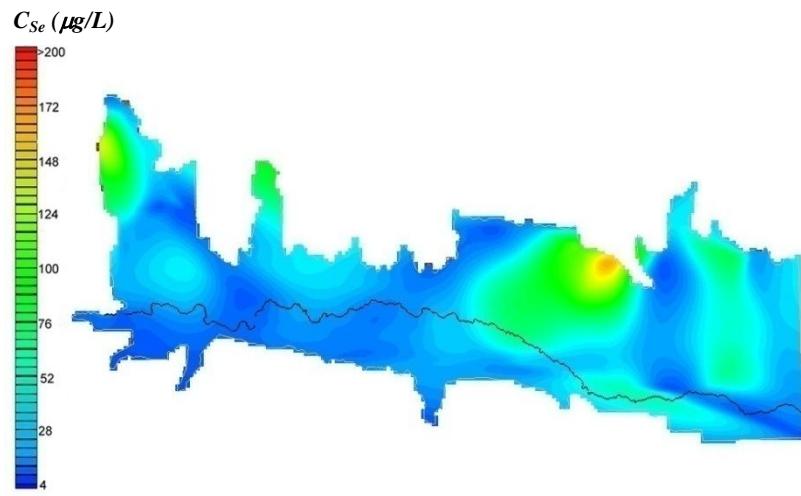


Figure G.35. Contour plot of C_{Se} from samples collected during March 10-15, 2006 in the Downstream Study Region.

No C_U Data
During this Event

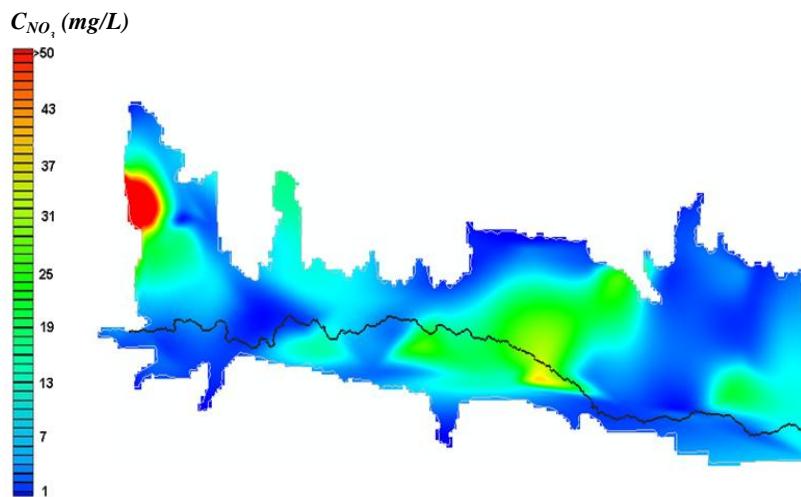


Figure G.36. Contour plot of C_{NO_3} from samples collected during March 10-15, 2006 in the Downstream Study Region.

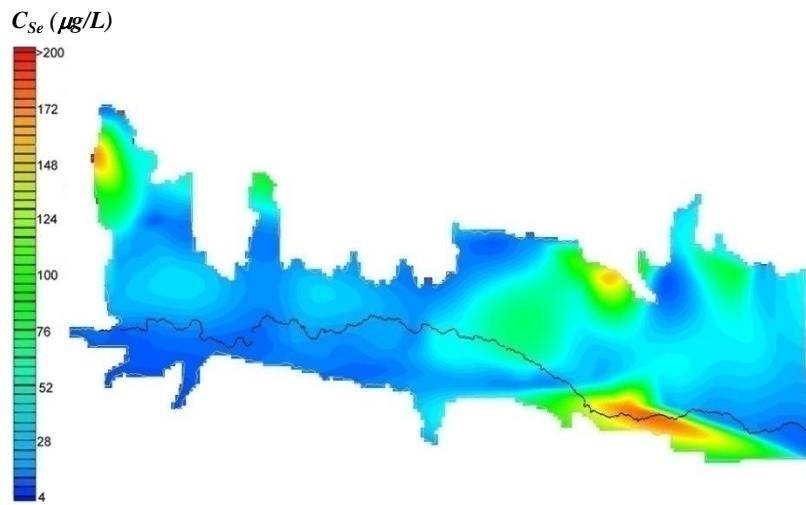


Figure G.37. Contour plot of C_{Se} from samples collected during May 13-17, 2006 in the Downstream Study Region.

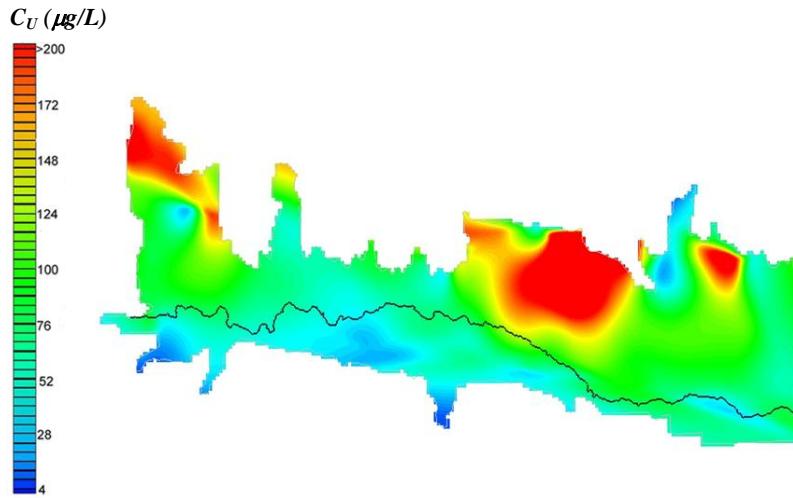


Figure G.38. Contour plot of C_U from samples collected during May 13-17, 2006 in the Downstream Study Region.

No C_U Data
During this Event

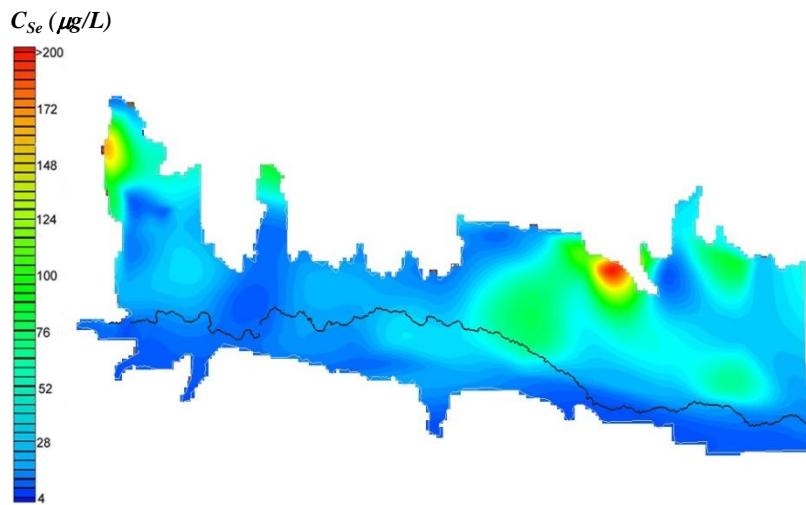


Figure G.39. Contour plot of C_{Se} from samples collected during June 12-16, 2006 in the Downstream Study Region.

No C_U Data
During this Event

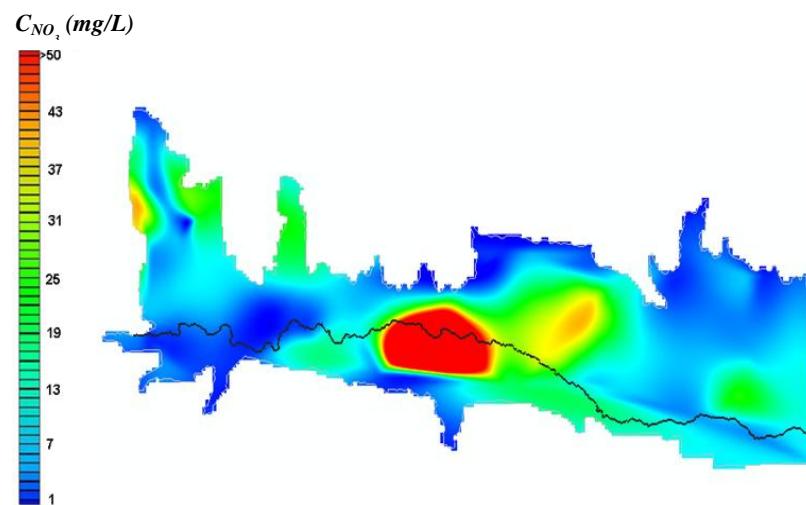


Figure G.40. Contour plot of C_{NO_3} from samples collected during June 12-16, 2006 in the Downstream Study Region.

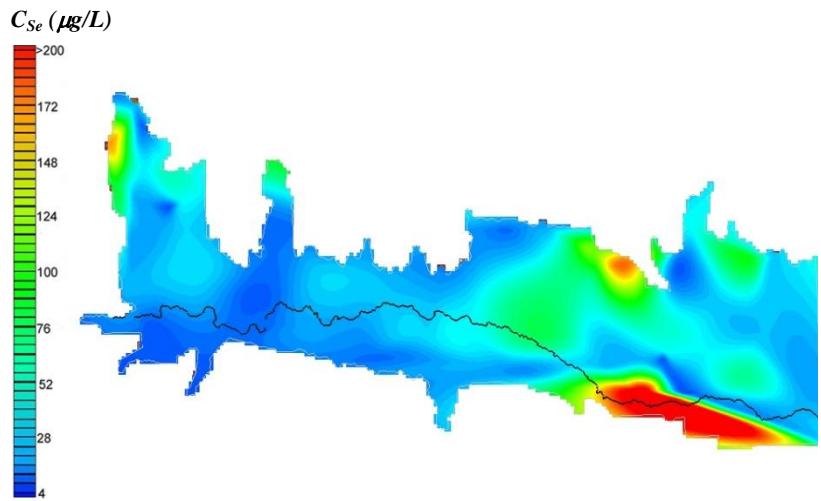


Figure G.41. Contour plot of C_{Se} from samples collected during July 10-13, 2006 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

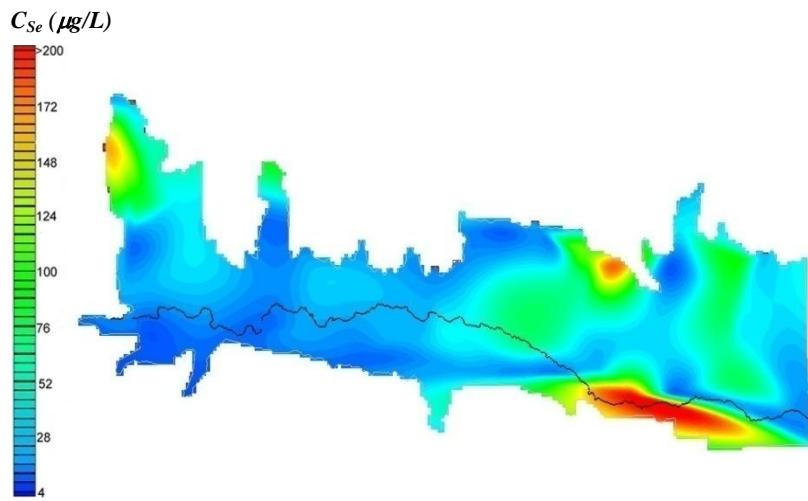


Figure G.42. Contour plot of C_{Se} from samples collected during August 7-10, 2006 in the Downstream Study Region.

No C_U Data
During this Event

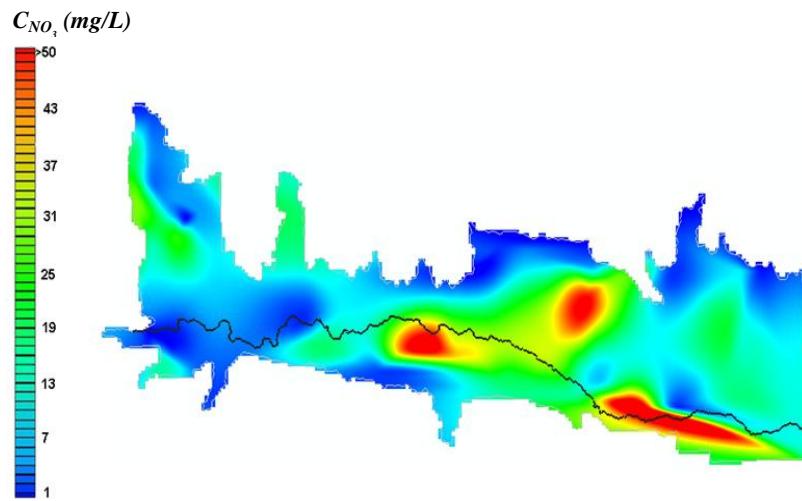


Figure G.43. Contour plot of C_{NO_3} from samples collected during August 7-10, 2006 in the Downstream Study Region.

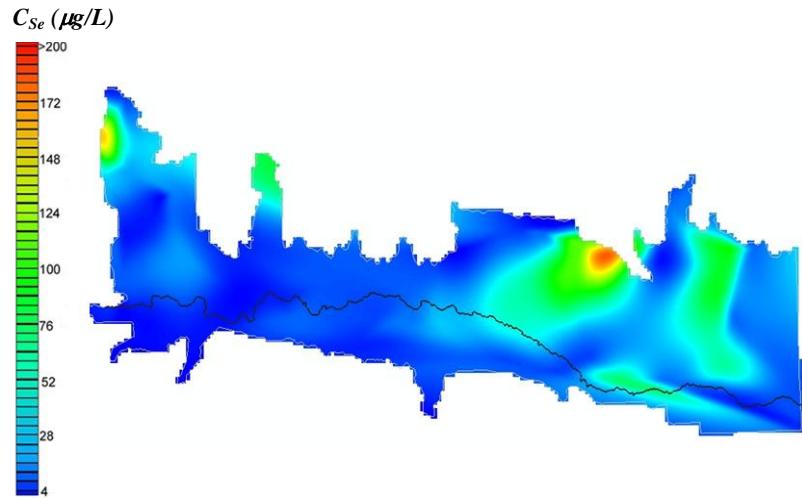


Figure G.44. Contour plot of C_{Se} from samples collected during November 18-20 2006 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

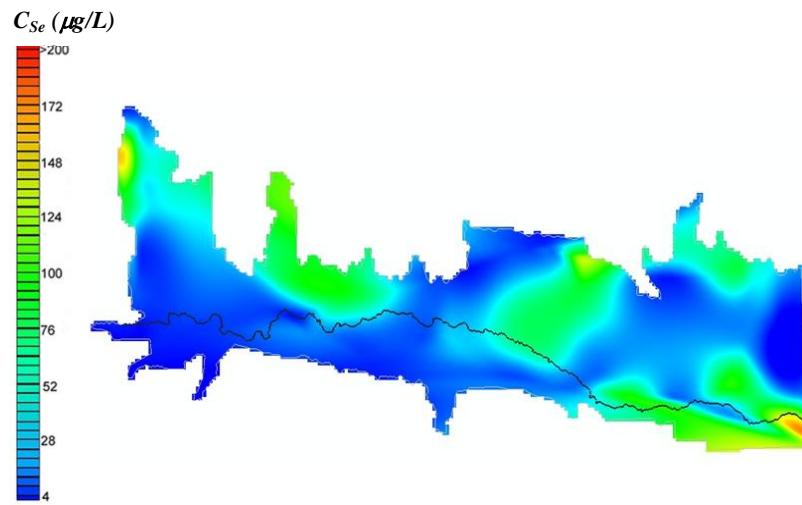


Figure G.45. Contour plot of C_{Se} from samples collected during March 9-11, 2007 in the Downstream Study Region.

No C_U Data
During this Event

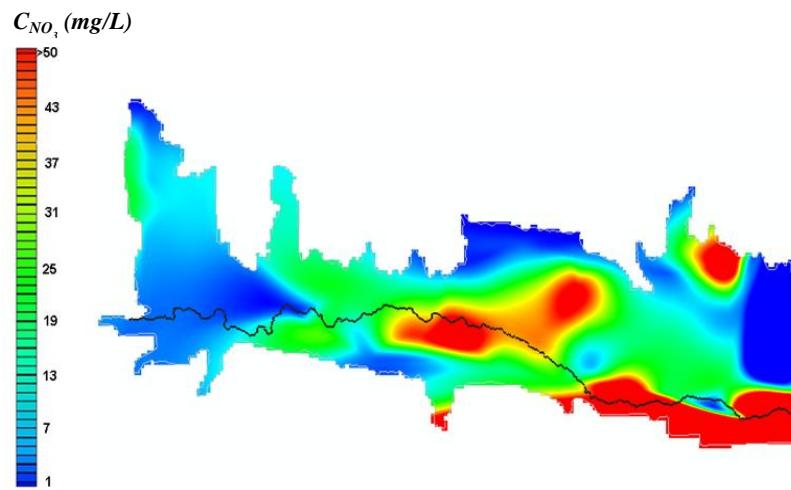


Figure G.46. Contour plot of C_{NO_3} from samples collected during March 9-11, 2007 in the Downstream Study Region.

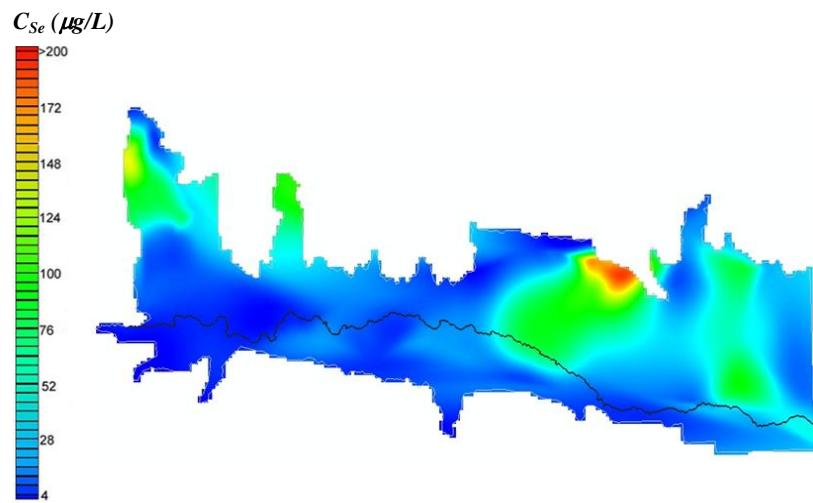


Figure G.47. Contour plot of C_{Se} from samples collected during May 15-18, 2007 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

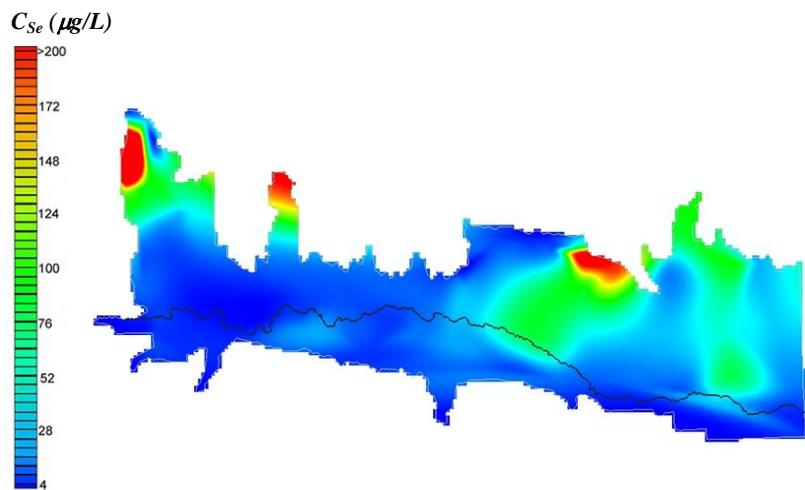


Figure G.48. Contour plot of C_{Se} from samples collected during June 18-22 2007 in the Downstream Study Region.

No C_U Data
During this Event

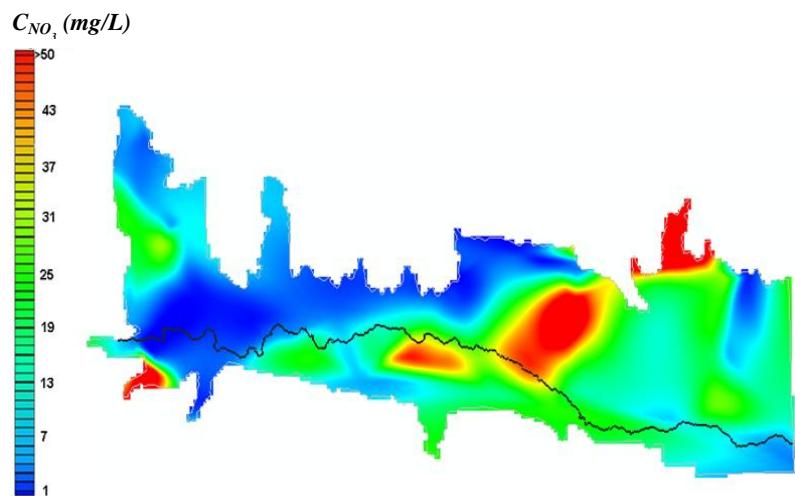


Figure G.49. Contour plot of C_{NO_3} from samples collected during June 18-22 2007 in the Downstream Study Region.

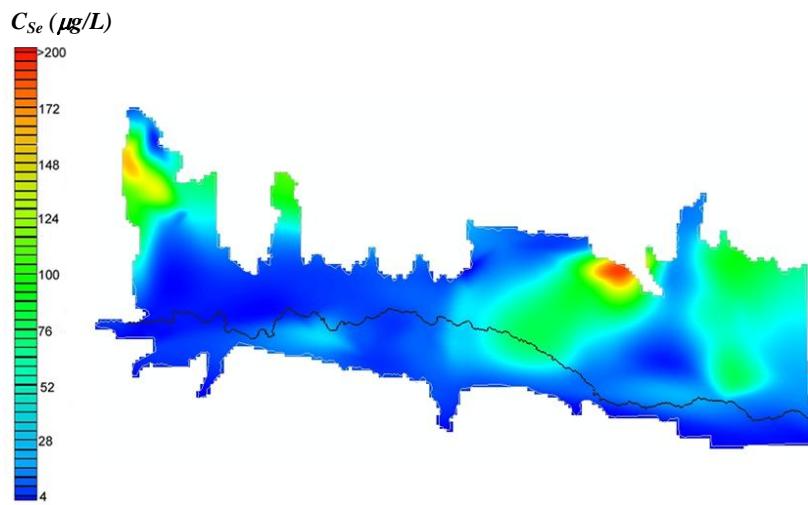


Figure G.50. Contour plot of C_{Se} from samples collected during July 22-24 2007 in the Downstream Study Region.

No C_U Data
During this Event

No C_{NO_3} Data
During this Event

APPENDIX H – L_s Values for Each Monitoring Well

Downstream Well L_s Values						Upstream Well L_s Values					
301	> 15,000	332	> 15,000	362A	1,838	1	2,988	37	> 15,000	78	321
301A	> 15,000	333	> 15,000	363	> 15,000	2	739	38	> 15,000	79	9,034
302	> 15,000	334	5,864	363A	5,161	5	575	39	4,567	80	3,255
303A	> 15,000	335	> 15,000	364	2,180	6	1,180	40	> 15,000	81	2,435
304	> 15,000	336	> 15,000	365	3,016	7	2,417	41	> 15,000	82	2,843
304A	> 15,000	337	> 15,000	366	4,440	8	910	42	14,923	83	> 15,000
305	> 15,000	338	> 15,000	368	> 15,000	9A	186	43	> 15,000	84	> 15,000
306	> 15,000	339	2,336	369	> 15,000	9B	-	45	> 15,000	85	> 15,000
306A	> 15,000	340	> 15,000	371	> 15,000	11	1,259	48	> 15,000	86	2,078
306AA	> 15,000	341	> 15,000	372	> 15,000	12	-	49	5,172	87A	> 15,000
307	> 15,000	342	> 15,000	373	> 15,000	13	6,073	50	14,111	87B	> 15,000
307A	> 15,000	343	> 15,000	375	> 15,000	14	503	51	-	88	3,620
308A	> 15,000	344	1,103	375G	> 15,000	15	5,370	52	16,958	90	> 15,000
312AA	> 15,000	345	3,144	376	6,270	16A	3,422	53	> 15,000	91	9,070
312b	> 15,000	346b	4,054	376A	> 15,000	16B	3,929	54	> 15,000	92	> 15,000
314	> 15,000	347	> 15,000	378	> 15,000	16C	4,341	55	6,955	93	3,083
315	> 15,000	348	> 15,000	379	> 15,000	17	4,165	59	> 15,000	94	5,865
316	> 15,000	349	5,251	380	> 15,000	18	381	60A	> 15,000	95	3,546
317b	> 15,000	350A	2,045	383	> 15,000	20	3	60B	1,970	96	3,831
318	> 15,000	350B	> 15,000	385	> 15,000	21	448	61	3,070	97	10,434
319A	3,858	350C	> 15,000	387	> 15,000	22	506	62	> 15,000	98	1,100
320	2,289	351	> 15,000	388	> 15,000	23	1,873	64	5,401	99	5,652
321	3,621	352	> 15,000	389	> 15,000	24	3,773	65	2,534	100	6,100
322	> 15,000	353	4,106	390	> 15,000	26A	> 15,000	66	620	200	2,067
323	> 15,000	354	> 15,000	391	> 15,000	26B	96	67	1,248	201	567
324	> 15,000	356	> 15,000	392	> 15,000	27	> 15,000	68	1,151	202	1,316
325	> 15,000	357	> 15,000	393	> 15,000	28	> 15,000	69	521	203	3,455
326	> 15,000	358	> 15,000	397	701	29	2,186	70	1,695	204	2,810
327	> 15,000	359	> 15,000	398a	1,298	30	2,186	71	818	205	2,810
328	> 15,000	359J	> 15,000	400	1,066	31	6,849	72	454	206	718
329	> 15,000	361	4,241	401	> 15,000	32	6,849	73	1,996	207A	436
330	5,637	362	4,462	MBC_W3	> 15,000	33	2,242	74	2,652	207B	344
						34	> 15,000	75A	71	208	1,735
						35	1,998	75C	49	209	635
						36A	5,284	76	6,713		
						36B	6,365	77	4,152		